Department of Energy Techology

FUTURE COMBUSTION TECHNOLOGY FOR SYNTHETIC AND RENEWABLE FUELS IN COMPRESSION IGNITION ENGINES (REFUEL)

Final Report

Päivi Aakko-Saksa, Anders Brink, Matti Happonen, Juha Heikkilä, Tuomo Hulkkonen, Matteo Imperato, Ossi Kaario, Päivi Koponen, Martti Larmi, Kalle Lehto, Timo Murtonen, Teemu Sarjovaara, Aki Tilli, Esa Väisänen

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Abstract

This domestic project, Future Combustion Technology for Synthetic and Renewable Fuels in Compression Ignition Engines (ReFuel), was part of a Collaborative Task "Future Combustion Technology for Synthetic and Renewable Fuels in Transport" of International Energy Agency (IEA) Combustion Agreement. This international Collaborative Task is coordinated by Finland. The three-year (2009-2011) project was a joint research project with Aalto University (Aalto), Tampere University of Technology (TUT), Technical Research Centre of Finland (VTT) and Åbo Akademi University (ÅAU). The project was funded by TEKES, Wärtsilä Oyj, Neste Oil Oyj, Agco Sisu Power, Aker Arctic Technology Oy and the research partners listed above.

Modern renewable diesel fuels have excellent physical and chemical properties, in comparison to traditional crude oil based fuels. Purely paraffinic fuels do not contain aromatic compounds and they are totally sulphur free. Hydrotreated Vegetable Oil (HVO) was studied as an example of paraffinic high cetane number (CN) diesel fuels.

HVO has no storage and low temperature problems like the fatty acid methyl esters (FAMEs) have. The combustion properties are better than those of crude oil based fuels and FAME, because they have very high cetane numbers and contain no polyaromatic hydrocarbons (PAH). With low HVO density, viscosity and distillation temperatures, these advantageous properties allow far more advanced combustion strategies, such as very high exhaust gas recirculation (EGR) rates or extreme Miller timings, than has been possible with current fossil fuels. The implementation of these advanced combustion technologies, together with the novel renewable diesel fuel, brought significant nitrogen oxides (NOx), particulate matter (PM) emission reductions with no efficiency losses.

The objective of ReFuel project was to develop new extremely low emission combustion technologies for new renewable fuels in compression ignition engines. The target was to decrease emissions at least by 70%. The scope was to utilize the physical and chemical properties of the renewable fuels that differ from properties of the traditional crude oil based fuels and to develop optimum combustion technologies for them. The project focused firstly, on paraffinic high cetane number fuels i.e. hydrotreated vegetable oil fuel as a typical representative of this kind of fuel and secondly, on fuels with high content of oxygenates. This was implemented by blending oxygenate to HVO fuel.

Keywords diesel engines, emissions, efficiency, alternative fuel, paraffinic fuel, HVO, synthetic fuel, Cetane number, EGR, Miller cycle, oxygenate

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Table of contents

1. Introduction

This domestic project, Future Combustion Technology for Synthetic and Renewable Fuels in Compression Ignition Engines (ReFuel), was part of a Collaborative Task "Future Combustion Technology for Synthetic and Renewable Fuels in Transport" of International Energy Agency (IEA) Combustion Agreement. This international Collaborative Task is coordinated by Finland. The three-year (2009-2011) project was a joint research project with Aalto University (Aalto), Tampere University of Technology (TUT), Technical Research Centre of Finland (VTT) and Åbo Akademi University (ÅAU). The project was funded by TEKES, Wärtsilä Oyj, Neste Oil Oyj, Agco Sisu Power, Aker Arctic Technology Oy and the research partners listed above.

In the field of transport power units, the traditional diesel- and otto-cycles have been developed since late 19th century. The development work has aimed to optimize the processes for crude oil based gasoline and diesel fuel. The awareness of CO2 emissions' effect on the climate change and the limited resources of crude oil have brought the focus on the bioderived renewable fuels.

The novel renewable diesel fuels have excellent physical and chemical properties, in comparison to traditional crude oil based fuels. For example paraffinic fuels do not contain aromatic compounds and they are totally sulphur free. Fischer-Tropsch (FT) diesel fuel and Hydrotreated Vegetable Oil (HVO) are examples of paraffinic high cetane number (CN) diesel fuels.

These fuels do not have storage and low temperature problems, as the fatty acid methyl esters (FAMEs) have. The combustion properties of these novel fuels are in most cases better than those of crude oil based fuels, because

they have very high cetane numbers and zero polyaromatic hydrocarbons (PAH). These advantageous properties allow far more advanced combustion strategies than has been possible with current fossil fuels. The implementation of these advanced combustion technologies together with the novel renewable diesel fuels, allow us to reduce significantly nitrogen oxides (NO_x) emission without drawbacks on particle matter (PM) emissions or engine efficiency.

The objective of ReFuel project was to develop new extremely low emission combustion technologies for new renewable fuels in compression ignition engines. The target was to decrease emissions at least by 70%. The scope was to utilize the physical and chemical properties of the renewable fuels that differ from properties of the traditional crude oil based fuels and to develop optimum combustion technologies for them.

The project focused firstly, on paraffinic high cetane number fuels i.e. hydrotreated vegetable oil fuel as a typical representative of this kind of fuel and secondly, on fuels with high content of oxygenates. This was implemented by blending oxygenate to HVO fuel.

The project consisted of following research paths supporting each other's:

- Literature review and reaction scheme evaluations
- Fuel spray studies
- Emission mapping calculations
- Optimum combustion design with CFD
- Engine tests with a high-speed research engine, LEO
- Engine tests with a medium-speed research engine, EVE
- Extensive emission measurements
- Particle emission analysis
- Project reporting and analysis

The responsibilities for the research partners were divided as follows:

Aalto

- Fuels and emissions literary study
- CFD studies with PHI-T maps and piston shape optimization
- Medium-speed engine test runs
- High-speed engine test runs
- Gaseous emission during medium- and high-speed test runs

VTT

- Diesel oxygenate literary study
- Gaseous emission during high-speed engine test runs
- Particle emissions during high-speed engine test runs

ÅA

- Combustion reaction scheme analysis
- Emission mapping

TTY

- Particle emissions during the high-speed engine test runs

2. Fuels

2.1 Hydrocarbon fuels - literature (Aalto)

At the beginning of the project, a literature study on paraffinic fuel characteristics and previous high CN paraffinic diesel fuel studies was made. This was in order to get a comprehensive picture of the potential of the fuel used, to get a basis for the oxygenate fuel choice and to lay the foundation for planning engine test runs. The main findings of the literature study were published at 2010 CIMAC congress in Bergen. (See Tilli, A. et al., 2010).

In the study, it was found that paraffinic high cetane number diesel fuels have been quite widely studied (see figure 2.1), but mainly without engine parameter optimization or modern emission reduction technologies. With no aromatics or sulfur, having a purely paraffinic nature, the fuels burn very cleanly and thoroughly and as such diminish emissions, especially soot compared to standard diesel. Some studies have combined high EGR (exhaust gas recirculation) rates and paraffinic fuels, thus reaching up to 70% reductions in PM or NO_x emissions, separately. No combined high cetane number fuel and very advanced Miller timing studies were found.

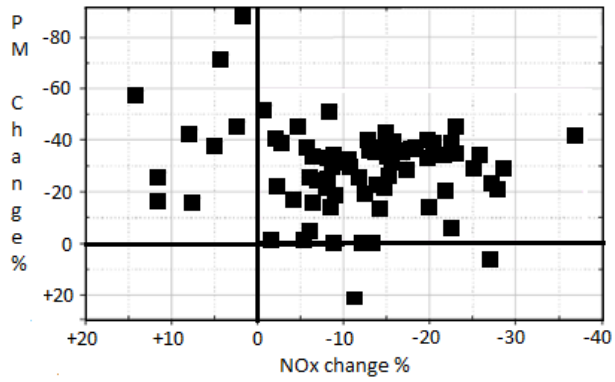


Figure 2.1. NO_x and PM reduction summary of previous paraffinic diesel fuel studies. (Alleman et al. 2003)

In the literature study, the possibility to achieve extremely low emissions with modern paraffinic diesel fuel was highlighted. The physical properties (see Table 2.1) of paraffinic diesel, such as low density, bulk modulus, viscosity and distillation temperatures promote wide fuel spray angles, smaller droplets in the fuel spray, early evaporation and thus short liquid penetration, which leads to good mixing and less spray-wall interactions. This reduces PM, HC and CO emissions. In order to enhance mixing even further, advanced injection timing can be used. However, while reducing PM, this may increase NO_x emissions. To improve the already very stable paraffinic fuel combustion, pilot injection strategy may be used.

Table 2.1. Typical properties of HVO, European EN 590:2004 diesel fuel, GTL and FAME. (Aatola et al. 2008)

	HVO	EN 590 (summer grade)	GTL	FAME (from rape seed oil)
Density at 15 °C (kg/m^3)	775 ... 785	≈ 835	770 ... 785	≈ 885
Viscosity at 40 °C (mm^2/s)	2.5 ... 3.5	≈ 3.5	3.2 ... 4.5	≈ 4.5
Cetane number	≈ 80 ... 99	≈ 53	≈ 73 ... 81	≈ 51
Distillation range (°C)	≈ 180 ... 320	≈ 180 ... 360	≈ 190 ... 330	≈ 350 ... 370
Cloud point (°C)	−5 ... −25	≈ −5	−0 ... −25	≈ −5
Heating value, lower (MJ/kg)	≈ 44.0	≈ 42.7	≈ 43.0	≈ 37.5
Heating value, lower (MJ/l)	≈ 34.4	≈ 35.7	≈ 34.0	≈ 33.2
Total aromatics (wt-%)	0	≈ 30	0	0
Polyaromatics (wt-%)[(1)]	0	≈ 4	0	0
Oxygen content (wt-%)	0	0	0	≈ 11
Sulfur content (mg/kg)	< 10	< 10	< 10	< 10
Lubricity HFRR at 60 °C (µm)	< 460[(2)]	< 460[(2)]	< 460[(2)]	< 460
Storage stability	Good	Good	Good	Very challenging

[(1)] European definition including di- and tri+ -aromatics
[(2)] With lubricity additive

According to some studies, the high cetane number may cause even increased PM emissions in the combustion chamber, due to short mixing and premixed combustion. However in the case of high EGR rates or very advanced Miller timing, the high equivalence ratio conditions prevent short ignition delays. On the contrary, high CN means better ignition and complete combustion in difficult combustion conditions, and thus reduces PM, HC and NO emissions and allows higher EGR rates to diminish NO_x emissions. According to some sources, with lower compression ratio, the NO_x -PM trade-off curve was found to more beneficial. Therefore, Miller cycle was later used to decrease the effective compression ratio without affecting the expansion ratio.

By blending oxygenates with the paraffinic fuel, the combustion is enhanced especially in rich zones and thus PM emissions can be further reduced. A possible lower combustion temperature (with some oxygenates) may decrease also NO_x emissions.

2.2 Cold properties of paraffinic high CN diesel fuels – literature (Aalto)

At the moment there is very little published material considering cold properties of HVO and information is quite scattered. Some research has been made about cold properties of Fischer-Tropsch fuels, which are chemically so similar to HVO, that those results can be used to evaluate also HVO's cold properties.

Cold properties of these fuels can be evaluated in same manner as in light fuel oils and automotive diesels. This is done with few characteristics, most important ones being cloud point and CFPP. It is important to notice, that paraffinic diesel fuel's cloud point and CFPP are almost identical, unlike with fossil diesel fuel. This means that operability at low temperatures is quite easily evaluated simply by cloud point.

Cold properties of HVO and F-T fuels are excellent. Cloud point is adjustable at refining phase by changing process parameters. In this way, cloud point can be set as low as -40 °C. Field tests have been made at various locations and with both blended and neat fuel. All these tests gave encouraging results, as no fuel related problems occurred. This proves that evaluation of operability can be reliably made with just cloud point, which was in tests selected carefully.

The full literature study titled "Paraffinic High Cetane Number Diesel Fuels in Arctic Conditions" can be found as appendix 1.

2.3 Diesel oxygenates – literature (VTT)

Oxygenates are considered as diesel fuel components, because they are capable of reducing exhaust emissions, especially as concerns particulate matter emission. Oxygenates based on the renewable feedstocks would also help with climate change and energy security challenges. The optimum oxygenate would be compatible with unmodified compression-ignition engines and infrastructure. New engine technologies could allow usage of wider scale of oxygenates, but this aspect was excluded from the report at hand.

For diesel engine, NO_x and particulate matter emissions are bottlenecks. A combination of modified diesel fuel, oxygenate and emission control technologies might result in an optimum emission performance. Many fuel properties, both physical and chemical, are important parameters as regards exhaust emissions. The fuel properties of oxygenates depend on, e.g., length and type of alkyl chains. Oxygenates with higher molecular weight often have higher density, higher boiling point, higher viscosity, better lubricity, lower volatility, and lower flammability than respective oxygenates with lower molecular weight. Regulations and standards controlling diesel fuel quality should met even when oxygenates are used as blending components.

The objective of this study was to cover oxygenates, which are compatible with conventional diesel engines, and which can effectively reduce particulate matter emissions. Finally, one oxygenate was selected for the experimental part of the project. Production aspects are important when feasibility of oxygenates are evaluated. However, this aspect was excluded in this study.

The full literature study titled" Diesel oxygenates – literature and selection" can be found in appendix 2.

2.3.1 The effect of oxygenates on particulate matter emission

Various studies have shown that oxygenates reduce particulate matter (PM) emissions from diesel engines, for example *1 wt-% oxygen content of fuel have resulted in 3-15% and even 67% reductions* in PM emissions (Gonzales *et al.* 2001, Hess *et al.* 2000, Chang *et al.* 1997, Karas *et al.* 1994). A number of mechanisms have been presented to explain the effect of oxygen on PM emission. A general theory is that oxygenated fuels bring *oxygen in the combustion process*, which reduces soot formation. (Delfort *et al.* 2002). However, o*xygenates also change*

Particulate matter emissions reduce when fuel contains oxygen, but this is not a linear phenomenon.

- Functional group may overrule the effect of oxygen content.
- Engine, load and emission control characteristics are important parameters.

Favourable oxygenate chemistry:

- Short carbon chains.
- Linear carbon chains.
- Symmetrical position of oxygen in ethers.
- Cetane number, density, viscosity, distillation etc. are also important factors.

many chemical and physical properties of fuel. In addition, engine characteristics, load conditions and EGR settings may affect behaviour of oxygenates.

Delfort *et al.* 2002 concluded that the effect of oxygenate on the particulate matter emission depends primarily on the functional group, and within each functional group, oxygen content is a key parameter (Figure 2.2). Some low-oxygen fuels reduced particulate matter emission almost as much as the high-oxygen fuels. All oxygen containing compounds do not reduce PM emissions effectively, for example, aromatic 1-phenyl ethanol (Karas 1994).

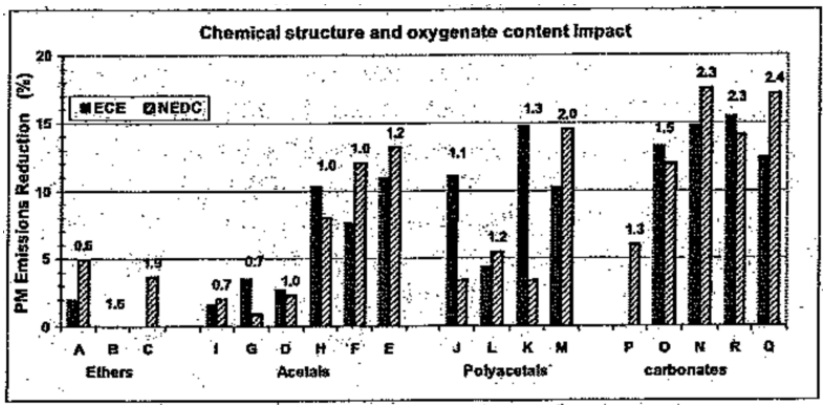


Figure 2.2. The effect of oxygen is important within each chemical group of oxygenates (Delfort et al. 2002).

In some studies lower soot emissions were observed for oxygenates in which each oxygen atom is connected to two carbon atoms (C-O-C, glycol ethers), but other studies have found O-C=O bond (esters, carbonates) more effective. One theory claims that C-O-C bonds are *efficient at premixed combustion*, whereas O-C=O bond *at mixing-controlled combustion*, which could explain different results depending on engine characteristics and test set-up. Some studies claim that molecules with C-O bonds remove one C per O atom, whereas esters remove one C per two O atoms (CO_2). Consequently, 30% of oxygen in ester would be unavailable for eliminating soot precursors. Other studies claim that strong oxygen-carbon bond (O-C=O) prevents carbon to involve efficiently into soot formation. In addition to oxygen in fuel, the role of *oxygen entrained from ambient is significant*. (Xu *et al.* 2006, Mueller *et al.* 2003, McCormic 2002, Yeh *et al.* 2001).

High cetane numbers generally lead to decreased ignition delay and higher combustion temperature. This may prevent increased particulate matter emission and other products of incomplete combustion, whereas NO_x emission may increase (Bertoli et al. 1997). However, no direct relation between oxygenate *cetane number* and particulate matter emission has been found (Delfort *et al.* 2002). In some cases, cetane number has been the determining fuel factor at lower loads, whereas oxygen content at higher loads (Nabi and Hustad 2010, Boot *et al.* 2007, Giavazzi *et al.* 1991). *Load* dependent behaviour of oxygenates might be related to changes in air-to-fuel ratio and combustion temperature (Boot *et al.* 2007). One study reported that the cetane number and oxygenates are important especially at high *EGR ratios*. Soot reduction efficiency has been reported to be at the highest for ethers when oxygen is in the middle of molecule, and for other oxygenates when carbon chain is short (McEnally and Pfefferle 2011).

As concerns hydrocarbons, paraffins have the highest cetane numbers. Typically, ignition quality improves as the chain length increases (Figure 2.3), and branching of the alkyl chain depresses. One study observed the highest cetane number for molecules with three ether groups in structure (e.g. glycols) (Pecci *et al.* 1991). *Cold flow properties* of oxygenates are dependent on, for example, chain length, branching and oxygen atoms. Certain mono-ethers may give the best compromise between cetane characteristics and the behaviour at low temperature. (Pecci *et al.* 1991).

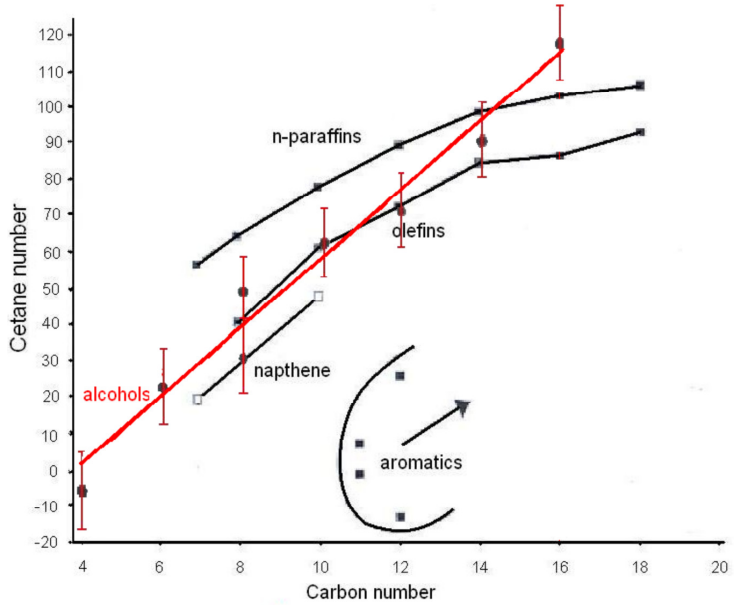


Figure 2.3. The effect of molecular size on CN (data: Shell Lexikon, Stournas et al. 1993).

Flash point is the limit temperature for the formation of an ignitable air-fuel vapor mixture. In Europe, flash point of diesel fuel must be higher than 55 °C. Fuel with lower flash point is stored and handled according to regulations of gasoline. New diesel components should fall into the *distillation range* of diesel fuel (around 180-340 °C) to ensure proper combustion of fuel.

Hydrocarbons are non-polar compounds with poor *water-solubility*. Water-affinity of oxygenates is typically higher than that of diesel fuel. This may increase phase separation risk, which is promoted at low ambient temperatures. In diesel engine, free water cause problems. Corrosion of materials may occur, as well.

Energy content of oxygenates is lower than that of hydrocarbon fuels, and this is seen in volumetric fuel consumption. Low *viscosity* of fuel may cause fuel leakages, whereas high viscosity of fuel may over-load the injection system. *Lubricity* may be problem for some many oxygenates, but it can be improved with additives. *Heat of evaporation* affect emissions, as well.

2.3.2 Oxygenate options

Table 2.2. The general structure of oxygenates.

R-OH	*Alcohols*
R-O-R	*Ethers*
R-O-R-O-R	*Glycol ethers*
R-O-C-O-R	*Acetals*
R-C(=O)-O-R	*Esters*
R-O-C(=O)-O-R	*Carbonates*

R, hydrocarbon chain; C, carbon; O, oxygen

Many studies have covered a comprehensive set of oxygenates including various alcohols, ethers, esters and carbonates (Table 2.2). The best-known diesel oxygenates at the moment are esters: fatty acid methyl esters, FAME. These oxygenates are extensively studied and reported. Glycerol is formed as a side-product in FAME production, and some glycerol derivatives can be candidates as diesel fuel components. (Di Serio *et al.* 2010, Boot *et al.* 2007).

Low-molecular weight alcohols, methanol and ethanol, are not suitable blending components for diesel fuel. However, neat ethanol with ignition improver additive can be used in modified diesel engines, for example in Scania's ethanol buses. (Aakko and Nylund 2004). Boiling points of butanol isomers are below 120 °C. With butanol addition, cetane number, lubricity, viscosity and flash point of diesel fuel may fall below requirements. (Wadumesthrige *et al.* 2010). *Heavy alcohols* are included in commercially available Swedish fuel (Agrodiesel 15). (Petterson 2005, Golubkov 2005). *2-Ethoxy ethanol* has been reported to be efficient in terms of exhaust emissions (boiling point 135 °C) (Subramanian *et al.* 2009). *Isodecanol* has been reported to be efficient oxygenate in reducing particulate matter emission at 2 wt-% oxygen level (Yeh *et al.* 2001).

Low-molecular weight ethers, e.g. dimethyl ether (DME), *diethyl ether* (DEE), *dimethoxymethane* (DMM) and *acetal* (1,1-dietoxyethane), are not considered in this study, because they require modifications in the fuel injection system of diesel engine. Boiling point of *di-n-butyl ether* (DBE, 141 °C) is close to the distillation range of diesel fuel, but flash point is very low (25 °C). (Beeckmann *et al.* 2010, Arteconi *et al.* 2011, Delfort *et al.* 2002).

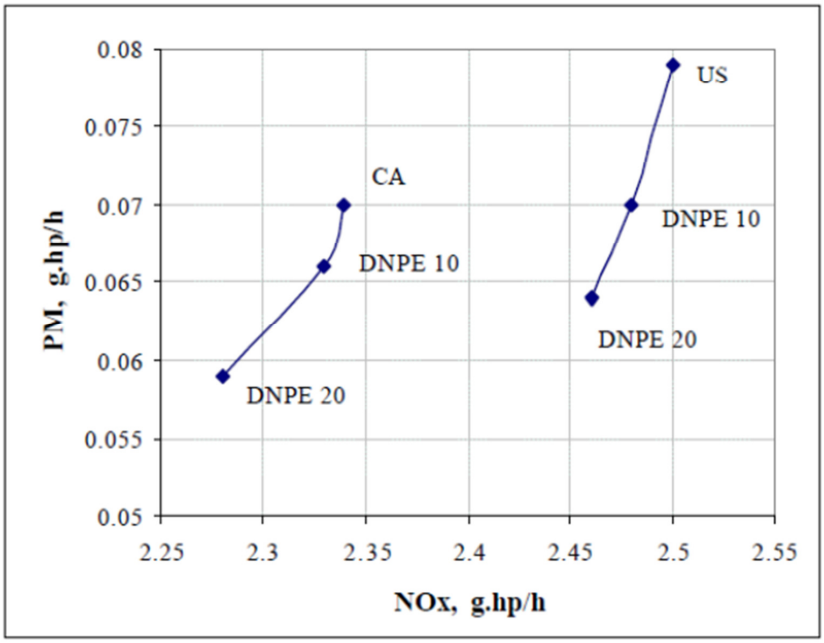


Figure 2.4. Trade-off between PM and NO_x emissions by using DNPE as diesel fuel component for the heavy-duty engine. (Marchionna 2000).

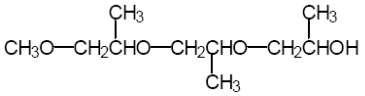
Di-n-pentyl ether (DNPE, C_5H_{11}-O- C_5H_{11}*)* has proved to be a potential oxygenate for blending into diesel fuel. Cetane number of *di-n-pentyl ether* (DNPE) is high (103-153) and other properties are diesel-like. DNPE is fully soluble in diesel fuel. Solubility of DNPE in water is low and it is more biodegradable than some other fuel ethers (e.g. MTBE). DNPE blends are reported to reduce PM, CO, HC, NO_x and air toxic emissions (Figure 2.4). Emission benefits were observed also under cold conditions. (Marchionna *et al.* 2000, Murphy 1999, 2002, Giavazzi 1991).

Poly-ethers are claimed to be good diesel fuel components. *Dibutoxymethane* (butylal, $C_9H_{20}O_2$) has a boiling point of 180 °C, flash point is 62 °C and cetane number over 74. In the engine tests, butylal reduced exhaust opacity and did not increase NO_x emission. (Bertola *et al.* 2000, Murphy 1999, 2002) *Di-n-pentoxy methane* (DNPM) has been also reported to be favourable fuel component. Boiling point of DNPM is 218 °C, and cetane number 97. Other properties of DNPM are diesel-like. Particulate matter emissions reduced with fuel containing DNPM when compared to diesel fuel. (Giavazzi 1991). *Diethoxy butane* is mentioned as an interesting diesel oxygenate, which has cetane number of 97, but low flash point (45 °C) (McCormick *et al.* 2002). Many acetals and polyacetals have shown significant particulate matter reductions at 1-2 wt-% oxygen content in blend.

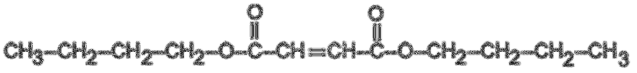
Monoglyme (*ethylene glycol dimethylether,* C-O-CC-O-C) and *diglyme* (*diethylene glycol dimethyl ether,* C-O-CC-O-CC-O-C) were earlier known as cetane improvers. These compounds have high oxygen content. Some *glymes* are addressed with problems in solubility, water tolerance or corrosion. Beneficial effect of *monoglyme* and *diglyme* on particulate matter and other exhaust emissions have been observed, but NO_x emission do not change or tends to increase. In one study, diglyme was best from six glycol offering 13% reduction in particulate matter emission, with 2.5% increase in NO_x emission. (Hess *et al.* 2000, Natarajan *et al.* 2001, Ren *et al.* 2007, Loganathan *et al.* 2007, Zhu *et al.* 2003, Kozak *et al.* 2007, Nabi and Hustad 2010).

One study reported that *tripropylene glycol monomethyl ether* (TPGME) and *dibutyl maleate* (DBM) (figure 2.5)are the most promising oxygenates from those having more than 35 wt-% oxygen content (Natarajan *et al.* 2001, Gonzáles *et al.* 2001). TPGME is miscible in aromatic diesel fuel, but addition of water may lead to phase separation. *Dibutyl maleate* (DBM) is soluble in diesel fuel. (Murphy 2002). Some studies find TPGME glycol

ether as more effective soot reduction agent than maleate, whereas other studies reported opposite results. One study included seven glycols, two maleates and two carbonates. *Diethyl maleate*, *dimethyl carbonate* and *diethyl carbonate* were selected as the most promising oxygenates. (Kozak *et al.* 2008a, 2009, Stoner and Litzinger 1999).



Tripropylene glycol monomethyl ether



Dibutyl maleate

Figure 2.5. Chemical structures of *tripropylene glycol monomethyl ether* (TPGME) and *dibutyl maleate* (DBM)

Dimethyl carbonate (DMC) is a low-molecular weight carbonate with boiling point of 90 °C. Boiling point of *diethyl carbonate* is higher, 127 °C, but still lower than distillation range of diesel fuel. *Diethyl carbonate*, has been reported to be soluble with diesel fuel, but having low flash point and high corrosivity. Solubility of *propylene carbonate* in diesel fuel is poor. *Dimethyl carbonate (DMC) has shown* a significant *reduction in exhaust particles*, and also a reduction in NO_x emission. Some tests indicated an increase in NO_x emissions. In one study, *diethyl carbonate* showed favourable NO_x/PM trade-off results. One study reported that *diethyl carbonate, dipentyl carbonate* and two *ether carbonates* resulted in some 12 to 17% reduction in PM emission. Generally, *carbonates showed higher reductions in particulate matter emissions than ethers and acetals*. (Arteconi *et al.* 2011) Subramanian *et al.* (2009) Kozak *et al.* (2008b, 2009) McCormick (2002) Keyu *et al.* (2002) Delfort *et al.* (2002) Karas (1994) Liotta *et al.* (1993).

In addition to over mentioned compounds, a number of other substancies have been as diesel components, for example, *2-ethoxy ethyl ether* (diethyl carbitol), *trioxane* and oligomerisation *"oxy-diesel"* products, cyclohexanone, 2-methoxyethyl acetate, di-isobutyl adibate, di-butyl phthalate, ethylene glycol mono-acetate, *2-ethoxyethyl carbonate* (MEEC)

amides and amines. (Delfort *et al.* 2002, McCormick *et al.* 2002, Murphy 1999, Hart Diesel Fuel News 2001, Lumpp *et al.* 2011, Boot *et al.* 2009, Yanfeng *et al.* 2007, Hilden *et al.* 2001, Lin and Huang 2003, Serdari *et al.* 2000, Stournas 1993, Guo *et al.* 2005).

All in all, favourable oxygenate chemistry for soot reduction has been presented in literature, but the conclusions are not consistent. This may be due to differences in engine characteristics, load conditions and EGR settings, which may affect behaviour and rating of oxygenates.

A comprehensive report on this matter is presented in appendix 2.

2.4 Fuels selected for the measurements

The fuel chosen to the future experimental studies was the hydrotreated vegetable oil NExBTL of Neste Renewable Fuels Oy. NExBTL has basically the same characteristics and physical properties as typical FT fuels, due to very similar composition. However, from the point of view of this research, NExBTL has the benefits of very high CN and slightly lower distillation range and viscosity, when compared with XTL fuels on the average. Besides the properties, other factors contributed to the fuel choice. NExBTL is familiar as a fuel, since it has been studied at Aalto Internal Combustion Engine research group previously. The fuel is also more available than other paraffinic fuels in Finland, especially in larger amounts needed during the extensive test runs.

Based on the literature, diesel fuel oxygenate was selected for the engine tests of the experimental part. In principle, a large number of oxygenates could be used as diesel fuel components. However, many oxygenates are addressed with end-use problems e.g. poor solubility with diesel fuel or safety problems. Economic feasibility of oxygenates was not discussed in this study.

The following criteria were used in the selection of diesel oxygenates for engine tests: cetane number minimum 51; flash point above 55 °C; boiling point close to 180-340 °C; soluble in diesel fuel. The target oxygen content of the blend in the experimental part was set to 2-3 wt-%. This means that components with oxygen content of 10 wt-% can be used without increasing blending ratio over 20%, for example. Almost 140 oxygenates were evaluated. Examples of the rejected oxygenates are dibutyl maleate (cetane

number below 50) and TPGME (phase separation risk). Some oxygenates, for example ethoxy ethyl ether and butylal, seemed interesting options, but they were not commercially available at the time of experiments.

Finally, di-n-pentyl ether (DNPE) was selected as oxygenate for the experimental part of "Refuel" project. DNPE performed well in the engine tests and emission behaviour was also good according to literature. Fuel properties of DNPE are diesel-like, and this oxygenate was also commercially available.

Oxygenated fuel in the experiments contained 2 wt-% oxygen, which was obtained by blending 20 wt-% DNPE and 80 wt-% HVO. Selected properties of the test fuels are shown in Table 3. Due to the low amount of oxygenated HVO available the test matrix was kept quite small. The reference load points of 50, 75, and 100 % were run. Also moderate EGR points of 2.5, and 5 % with 75 % load were run so the results could be compared with the EGR results using neat HVO.

Table 2.3 Selected properties of the test fuels

Quantity	Unit	EN 590	HVO	HVO + DNPE
EN590 diesel fuel	%-wt	100	0	0
HVO	%-wt	0	100	80
HVO + DNPE	%-wt	0	0	20
Density	kg/m^3	837,3	779,9	781,2
Viscosity (at 40°C)	mm^2/s	3,587	2,985	2,348
	MJ/kg	43,173	43,991	43,137
Eff. heating value	MJ/l	36,149	34,308	33,699
Cetane number (IQT)		54,7	88,2	93,9

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3. Combustion Analysis

3.1 Reaction scheme analysis (ÅA)

Commercial diesel fuels contain numerous chemical species, many of which no reaction schemes are available for. In addition, the fuel composition is not known in such a detail that a comprehensive description would be possible. In this project the fuel composition has been assumed to consist of a few model components, frequently used in the literature. The HVO fuel has been modelled using n-heptane as the model component. The EN590 has been assumed to consist of a mixture of n-heptane, to model the aliphatic fuel components, of benzene, to model simple aromatics and of naphthalene, to model aromatics with more than one ring.

Reaction mechanism of n-heptane, benzene and naphthalene are publicly available. E.g. Lawrence Livermore National Laboratory has published a number of kinetics schemes. However, for this project a mechanism developed by Naydenova was chosen as the starting point. In this mechanism the C_1-C_4 hydrocarbon oxidation mechanism originates from Hegesh, the C_2 mechanism from Wang and M. Frenklach. Reactions for C_3-, C_5- to C_8-hydrocarbons are based on the work of Richer and Howard, Skjoth-Rasmusseen et al. and Frenklach and Warnatz. The n-hepthane model has been adopted from Correa et al.

The formation and growth of polycyclic aromatic hydrocarbons is based on the HACA model by Frenklach et al. HACA is an abbreviation of H-abstraction C-addition. Additional reaction paths of PAH formation and growth for PAH between benzene and pyrene were adopted from Richter et al., together with several reaction paths for large polycyclic aromatics up to coronene. In this project, only soot precursors were modeled. Actual soot particles cannot be modeled as gas phase reactions. Usually a method of moments is used. Nevertheless, also in the growth of soot particles the HACA mechanism is assumed in addition to coagulation of particles.

Typically also the reaction rates are assumed to be similar for the soot reactions as for the soot precursor reactions.

To also be able to predict nitrogen chemistry, the mechanism of Naydenova was in this project extended with a set of reaction describing nitrogen chemistry from Coda Zabetta et al. These reactions are available from the Åbo Akademi web. In the literature, there are some updates to the nitrogen chemistry available. The complete mechanism contains 238 species and 1505 reactions. The subset describing the nitrogen chemistry consists of 194 reactions. In this project, also the nitrogen-chemistry mechanism by Mendiara and Glarborg has been investigated. In general, this reaction mechanism yields similar results. However, at low temperatures, i.e. around 1000K, this mechanism predicts formation of nitromethane (CH_3NO_2), a species not included in the mechanism by Coda Zabetta.

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3.2 Emission mapping (ÅA)

Phi-T maps have been used for some time, mainly to explain the trade-off difficulties between soot and NO_x, but also to obtain a deeper understanding for the chemistry. Phi-T maps are stationary, i.e., they do not represent a very detailed description of the combustion in the diesel process. Still, they are a way to include more complex chemistry than typically possible in CFD calculations.

3.2.1 Fuel composition

In the Phi-T map construction, three different fuel compositions were studied. The first composition was only n-hepthane. This pure paraffinic hydrocarbon was used as a model fuel for hydro-treated vegetable oil. Commercial diesel, EN590, was modelled using two different compositions. In the first, the maximum allowed aromatic fraction (30 w-%) was added as benzene (C_6H_6). In the second, the maximum aromatic content was retained, but the maximum allowed polyaromatic fraction was included as naphtalene ($C_{10}H_8$).

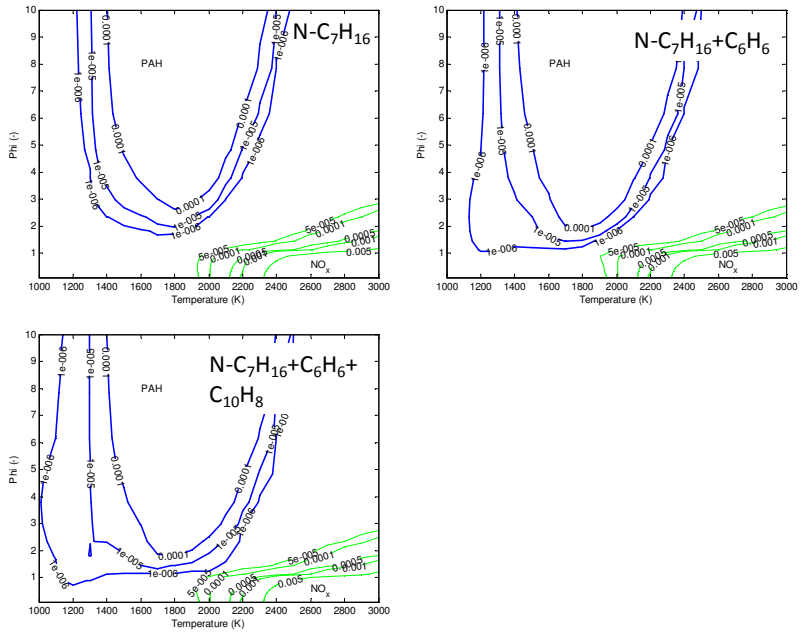


Figure 3.1. Phi-T maps showing PAH and NO_x for three different fuel compositions. The conditions used in the calculations are 80 bar and 1 ms residence time.

Figure 3.1 shows the Phi-T maps obtained in the three cases. From the figure it can be seen, that PAH, representing compounds with four to seven

aromatic rings, is larger when adding benzene or naphtalene. At low temperature, the EN590 is producing more PAH, but the level is low in this region. All cases shows a maximum in PAH yield around 1800K. According to the calculations the PAH yield has its maximum at a slightly lower temperature when aromatics are present in the initial fuel. In addition, adding aromatics to the fuel increases also the level in this region.

3.2.2 Exhaust gas recirculation

EGR is an effective way to lower the combustion temperature, and hence lowering NO_x emissions. In the ReFuel project Phi-T maps with different fractions and compositions of EGR have been constructed. The main objective has not been to study the effect of lowering the in-cylinder temperatures, but rather to study secondary effects of EGR. One focus has also been on possible differences between using real EGR and N_2, as done in the experimental part of this project. Figure 3.2 shows Phi-T maps for n-heptane with air and n-hephane with EGR, both using a exhaust gas with CO_2, H_2O, O_2 and N_2, resulting from use of EGR, and using only N2, but added in such a way that the same oxygen content of the charge air is obtained. In the calculations shown in Fig 5 the O2 content of the charge air in the EGR cases have been 18.5 w-%. The figure shows that the secondary effects of EGR and of the composition of EGR are small in this case. Nevertheless, the figure indicates that real EGR is chemically more reactive, resulting in a slightly lower PAH level and in a slightly higher NO_x level. In Figure 3.2 there is also a Phi-T map obtained adding NO and PAH to the charge air. In this figure all nitrogen containing species, except N_2, has been added and normalized by the NO in the charged are. This figure shows that the effect of including NO in the EGR may be important. All calculations for producing figure 3.2 have been carried out assuming 80 bar and 1 ms residence time.

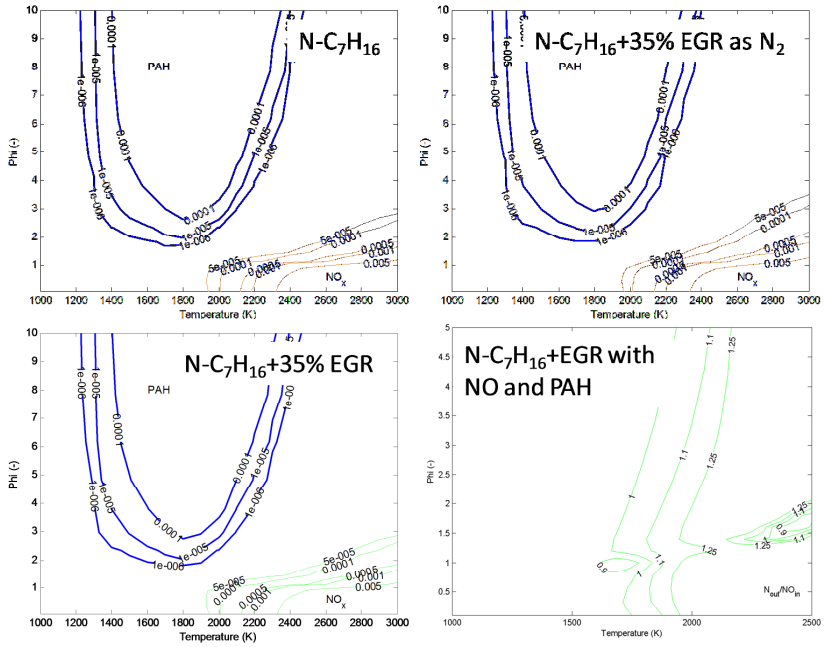


Figure 3.2. Phi-T maps showing the influence of exhaust gas recirculation and its composition. The conditions used in the calculations are 80 bar and 1 ms residence time.

3.2.3 Oxygenated fuels

Oxygenated compounds, here hydrocarbons containing oxygen, have raised some interest as a mean to suppress soot formation. In the ReFuel project engine tests were carried out using di-n-pentyl ether (DNPE). The chemical formula of this compound is $C_{10}H_{22}O$. On a mass base this compound contains approximately 10% oxygen. In the test runs, the fuel mixture had an oxygen content of approximately 2 w-%. No comprehensive reaction mechanism was available for this fuel. In the calculations for the Phi-T maps a mixture of n-heptane and methanol was used. However, the composition was chosen such that on a weight bases the mixture contained 2 w-% oxygen. To test the influence of the way the oxygen was supplied to the calculations, calculations were also carried out where O_2 was added to the fuel, such that the mixture contained 2 w-% O_2. Figure 3.3 shows the Phi-T maps for these cases. The figure shows that there is almost no effect of the oxygen in the fuel, neither of how the oxygen in the fuel is modeled. This result is not very surpising as the HACA-mechanism for PAH (and soot) growth do not involve reactions with oxygenated compounds. In the figure, also the result from a calculation with 25 w-% oxygen in the fuel

stream is shown. In this case, the PAH formation is clearly lower. However, this is most probably due to a very different fuel composition.

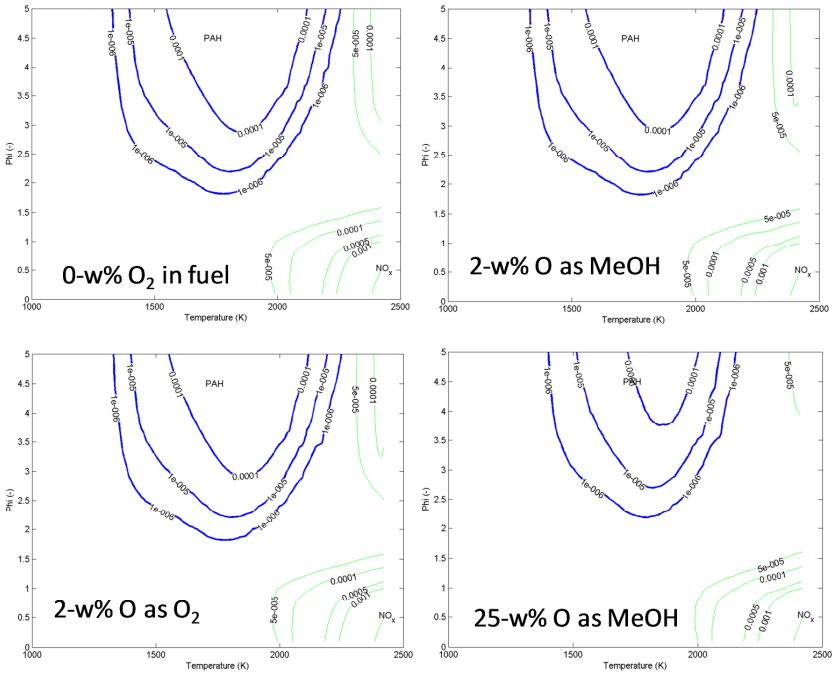


Figure 3.3. Phi-T maps showing the influence of the O-content of the fuel stream. The conditions in the calculations are 80 bar and 1 ms residence time.

3.2.4 Influence on Phi by fuel and charge air composition

The Phi-T maps of PAH and NO_x did not reveal large chemical differences between the various cases. Figure 3.4 shows the local Phi-value with HVO and the oxygenated blend used in the engine tests as a function of the local Phi-value using EN590. This calculation is performed assuming that the engine is run in an identical way with the different fuels, i.e., the fuel is changed but the amount of charge air and the volume of injected fuel is kept constant. In the calculations the following assumption has been made: EN590, $C_{12}H_{23}$, ρ=831 kg/dm³, M=167 g/mol, HVO, $C_{12}H_{26}$, ρ=784 kg/dm³, M=170 g/mol, and EN590+20% DNPE $C_{11.58}H_{22.79}O_{0.021}$, ρ=835 kg/dm³, M=165.12 g/mol. The figure shows that especially with the oxygenate blend, the local Phi-values in the different locations of the cylinder, during the combustion cycle are lower, i.e., less fuel rich conditions are prevailing. However, not only the local Phi will change when changing fuel, also the local adiabatic temperature. On the fuel rich side, an increased Phi-value will generally give rise to a higher combustion temperature. In addition, the different fuels will have different adiabatic combustion temperatures, which

also must be taken into consideration, especially when using these results to interpret the NO_x formation tendency. In the figure, corresponding results for an EGR case is also shown. This is a case with 18.5 w-% O_2 in the charge air. If the fuel injection is not adjusted, the EGR case will lead to more fuel rich conditions in the cylinder, since the oxygen content of the charge air is lower.

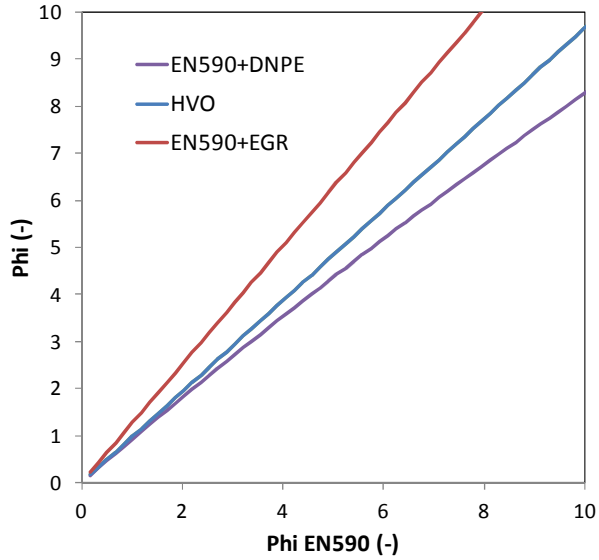


Figure 3.4. Phi for EN590 + di-n-pentyl ether, HVO, and EN590 in a EGR run as a function of Phi in a EN590 case assuming no modifications when switching fuel, i.e., volumetric injection and charge air pressure kept constant.

3.3 Phi-T Maps in Engine Combustion (Aalto, ÅA)

Equivalence ratio – temperature (Phi-T) maps have been investigated in high-speed engine conditions using 0% or 20% EGR rates. In engine measurements, pure N2 has been used for the EGR and hence also in simulations pure N2 has been used for EGR. The EGR rate has been defined as EGR rate = EGR mass / total mass. Assuming the EGR rate of 20% with pure N2 would be converted to "real" EGR including O2, CO2, and H2O, the EGR rate would be close to 38%. The simulation set up and engine operation point has been the same as in the Section "piston shape optimization", i.e. 1500 rpm and 50% load. Figure 3.5 shows the used mesh and the injection boundary condition.

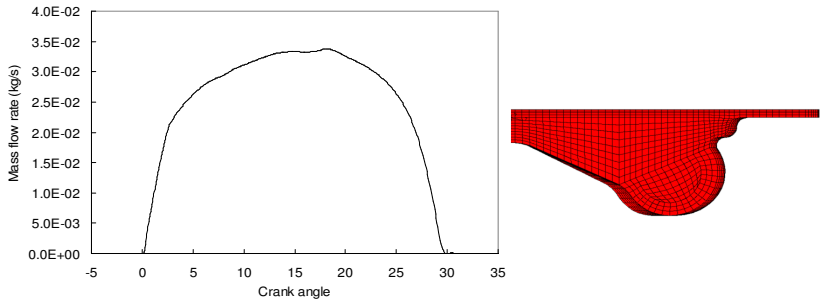


Figure 3.5. Calculated mass flow rate at the nozzle exit (left), and computational mesh for the standard Agco Sisu Power sector model piston (right).

Figure 3.6 shows the experimental soot and NO_x results using either 0% or 20% EGR rates (pure N2). This will be later compared to simulation results.

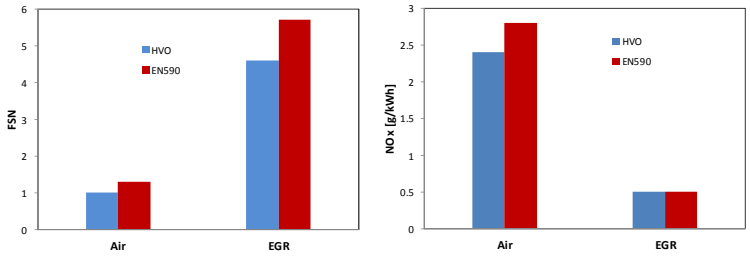


Figure 3.6. Measured NO_x and soot (FSN) emissions with either 0% or with 20% EGR. The EGR used has been pure N2 in the engine test.

Figure 3.7 shows the measured and computed pressure curves and the heat release rates. Also the mean and maximum gas temperatures are shown. Lower heat release rate is observed with 20% EGR which leads to lower cylinder pressure. This is well in accordance with the general observations when increasing the amount of EGR in engines. In addition, it is observed that adding 20% EGR lowers the maximum temperatures by some 200K and has an effect also to the mean temperature. Furthermore, N2 as EGR compared to "real" EGR with O2, CO2, and H2O seems to behave relatively similarly concerning heat release rate and gas phase temperatures.

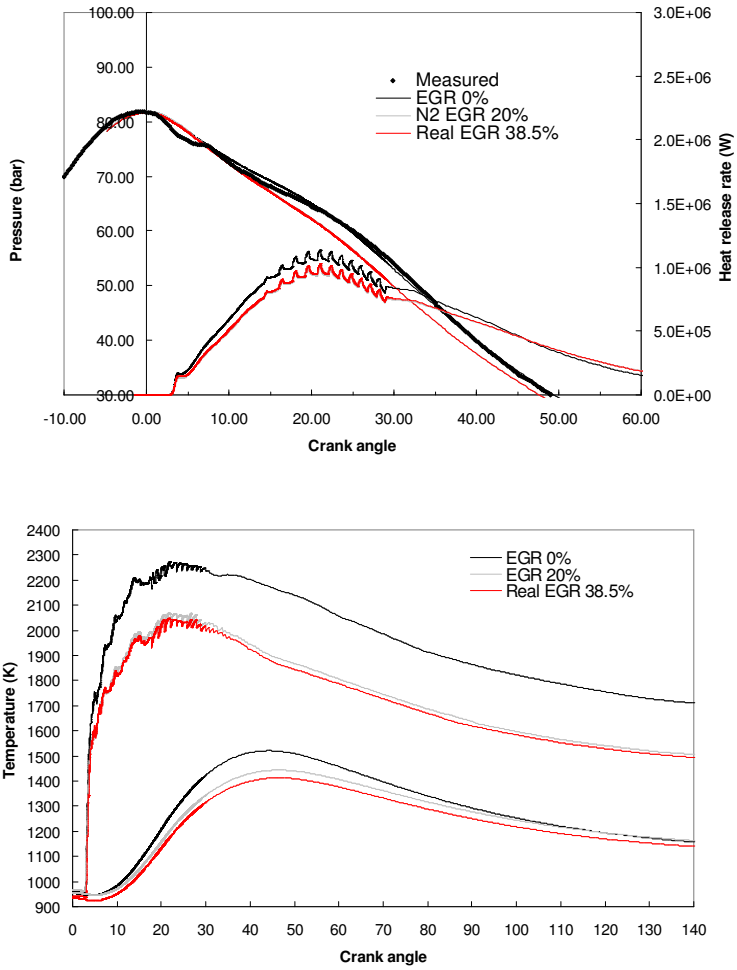


Figure 3.7. Measured and computed pressure curves together with heat release rate information (upper). Computed mean and maximum gas temperatures (lower). Measured pressure curve is with 0% EGR.

Figure 3.8 shows the computational result plotted to a Phi-T map. The Phi-T map has been created by detailed chemistry calculations with constant pressure and 2ms residence time. The effect of adding EGR can be clearly seen with lower temperatures. Hence, the computational points are moved in the EGR case to the left in the Phi-T map. This implies lower NO_x production but also lower soot production. In the figure 11 is shown a result from the simulations applying the Phi-T map combustion regimes with colors: red color indicates soot production area in the Phi-T map and green color indicates the favorable combustion area (low temperature combustion, LTC) where there is neither soot nor NO_x production according to the Phi-T map results. Because temperature is lower, the 20%

EGR case indicates lower soot production. As seen from the measurement data in the figure 3.6, this result is, however, contradictory to the experimental observations.

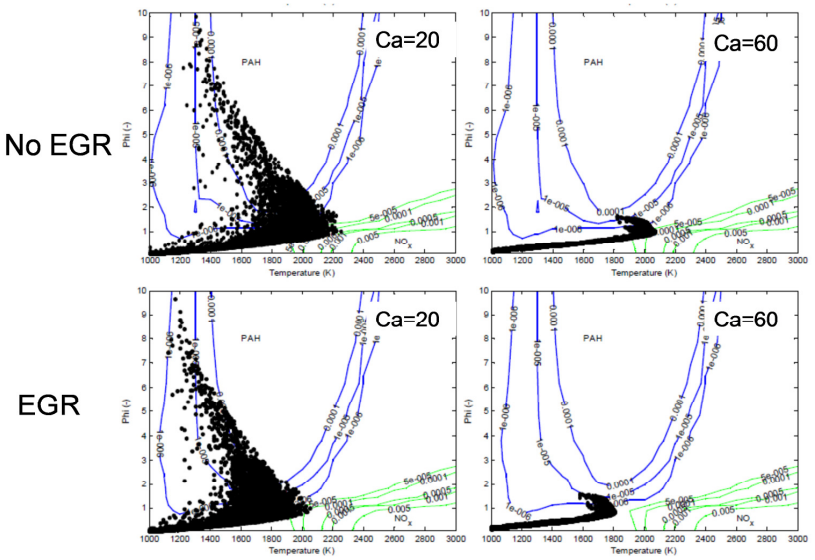


Figure 3.8. Simulation result plotted into Phi-T maps with different EGR rates. Result from two different crank angles (20 and 60 degrees after top dead center). Phi-T maps created by Anders Brink / Åbo Akademi.

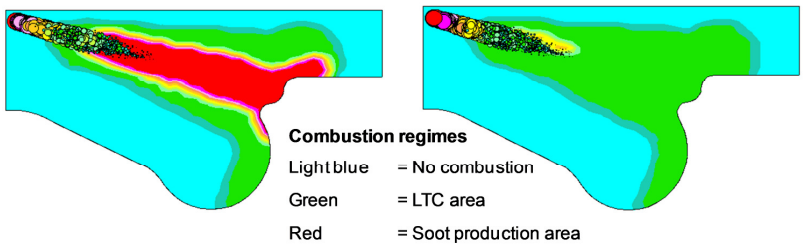


Figure 3.9. Local combustion environment in the combustion chamber according to Phi-T map regimes with 0% EGR (left) and 20% EGR (right). With the current engine operation point, the conditions do not reach high NO_x producing area.

3.3.1 Using Miller cycle in the simulations

Miller cycle was applied to the same engine operating point as shown above. The initial pressure at the intake valves closing was reduced from 1.72bar to 1.65bar and, at the same time, the initial temperature was lowered such that the mean gas temperature at the start of fuel injection

was 107K lower than in the normal cycle. This meant some 10% increase to the charge mass in the Miller case. Figure 3.10 shows the equivalent pressure and heat release data and the mean and maximum gas temperatures. It can be seen that combustion is proceeding in relatively similar fashion in both cases. However, in the mean temperature there is great difference that persists throughout the expansion stroke. This is a different type of behavior compared to the effect of EGR added to the intake air. Adding EGR lowers mostly the maximum temperatures whereas using the Miller cycle is mainly reducing the mean temperature. From figure 3.11 it is seen that according to the simulation, there is a large NO_x reduction due to the reduced mean temperature. On the other hand, the estimated soot emission is higher with the Miller cycle.

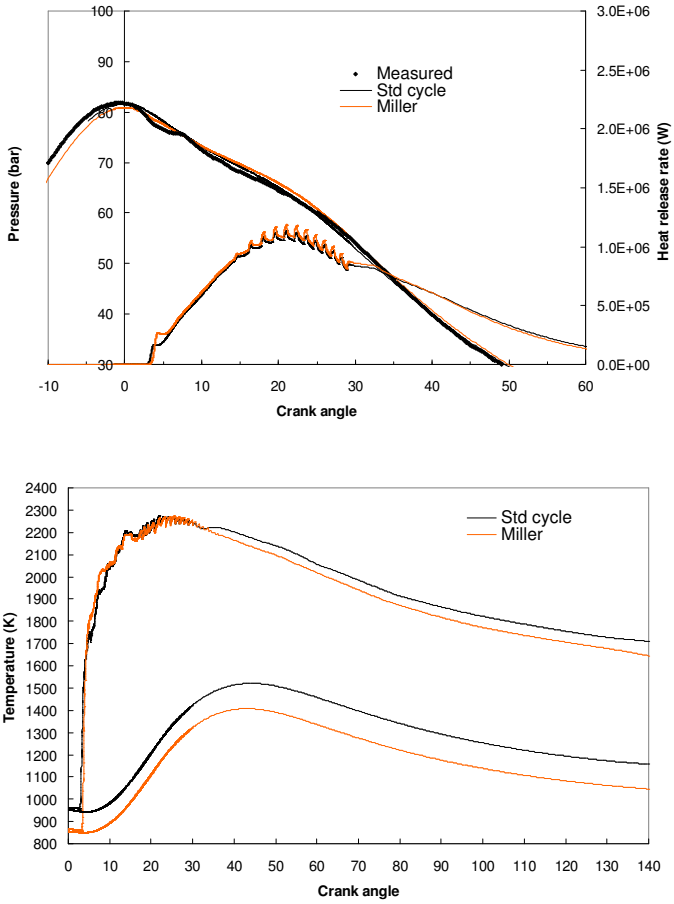
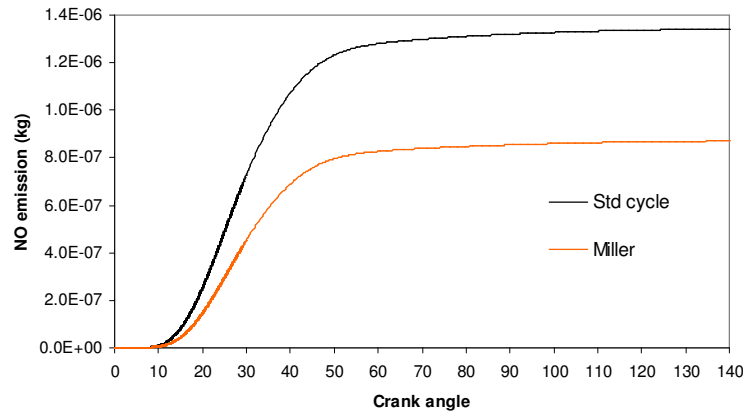


Figure 3.10. Measured and computed pressure curves in the normal cycle and in the Miller cycle together with heat release rate information (upper). Computed mean and maximum gas temperatures (lower).



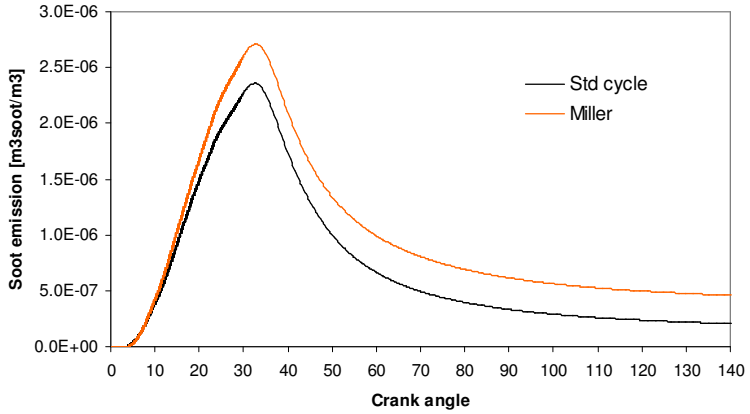


Figure 3.11. Computed NO_x (upper) and soot (lower) emissions in the normal cycle and in the Miller cycle.

3.3.2 Conclusions

CFD simulation results were plotted onto Phi-T maps which have been created with detailed chemistry simulations. It was observed that NO_x emissions can be well predicted by the Phi-T maps alone but it seems to be more difficult to predict soot emissions by only using the Phi-T map data. This is because soot oxidation and mixing are important processes but the Phi-T maps are not taking these into account. It was also observed that adding EGR reduces mainly the maximum gas temperatures during

combustion whereas the Miller technique reduces mainly the mean temperature and does not affect much the maximum temperatures. Despite the difference in the mechanism they affect the combustion temperatures, both methods are effective in reducing temperatures and hence NO_x. However, an optimum must be found for the amount of both EGR and Miller techniques used since soot emissions are increasing with higher EGR or Miller rates.

More information from these results can be found from the publications "Kaario Ossi, Brink Anders, Lehto Kalle, Keskinen Karri, and Larmi Martti, Studying Local Conditions in a Heavy-Duty Diesel Engine by Creating Phi-T Maps, SAE Technical Paper Series, 2011-01-0819, 2011" and "Kaario, O., Brink, A., Lehto, K., Keskinen, K., and Larmi, M., Studying Equivalence ratio – Temperature Maps in a Heavy-Duty Diesel Engine, Finnish-Swedish Flame Days 2011, Paper #16, 26-27.1.2011, Piteå, Sweden, 2011".

3.4 Piston shape optimization (Aalto)

CFD was used to find new piston shapes for optimization of the combustion process in terms of heat release rate, fuel consumption, and emission. The engine used for the study was a modified single cylinder version of the Agco Sisu Power's 84 CTA. The piston shape optimization was done at 50% load and at 1500 rpm engine conditions. The engine had 450bar injection pressure at this operating point with an 8-hole nozzle. The nozzle hole diameter was 0.162mm with a spray angle of 149 degrees (except the new design 2 with spray angle of 156 degrees). The mass flow rate at the nozzle exit was calculated with GT-Fuel by Karri Keskinen. The real start of the fuel injection was obtained from optical fuel spray measurements by M.Sc. Tuomo Hulkkonen. The mass flow rate at the nozzle exit and the computational sector mesh used for the standard Agco Sisu Power piston were previously shown in the figure 3.5.

The sector model had about 12700 computational cells at top dead centre. The k-e RNG turbulence model used was and the swirl number used for all the cases was 1.5. Ecfm-3z combustion model was used for all the cases.

3.4.1 Piston shapes tested

There were a total of 6 different variants in the computational piston shape tests. The variants were the new piston (nowadays the standard piston used in the engines), the old piston (a piston Agco Sisu Power has been using for a relatively long time before the new piston), new piston with protrusions, new piston design 1, new piston design 1.1, and new piston design 2. The different variants are shown in the figure 3.12.

The idea of including protrusions to the piston surface was the enhancement of fuel vapor mixing. The idea behind the new design 1 was to reduce combustion near the cylinder liner and to compare the effect of the relatively simple structure to that of the new piston's "wavy" surface. The new design 1.1 was tested after the results from the version 1.0 and the bowl was made shallower but somewhat longer. The idea of the new design 2 was to test traditional marine piston top shape in high speed engine conditions.

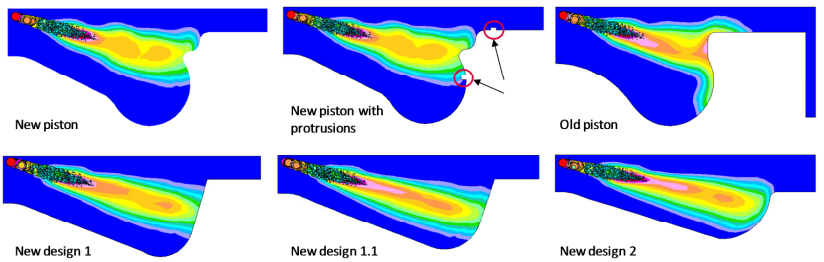


Figure 3.12. The piston shapes tested. Top left: new piston (standard piston used nowadays), top middle: new piston with protrusions, top right: old piston, bottom left: new design 1, bottom middle: new design 1.1, bottom right: new design 2. All piston shapes are shown at the crank angle 15 after top dead center. Red color indicates fuel mass fraction of 20% or more.

3.4.2 Results

Comparing the new piston, the old piston and the version with protrusions

Figure 3.13 shows the measured and computed pressure curves and the heat release rates. Also seen are the cumulative heats. It can be observed that the old piston has lower heat release rate during combustion but yet the cumulative heat is similar at the end of the simulation.

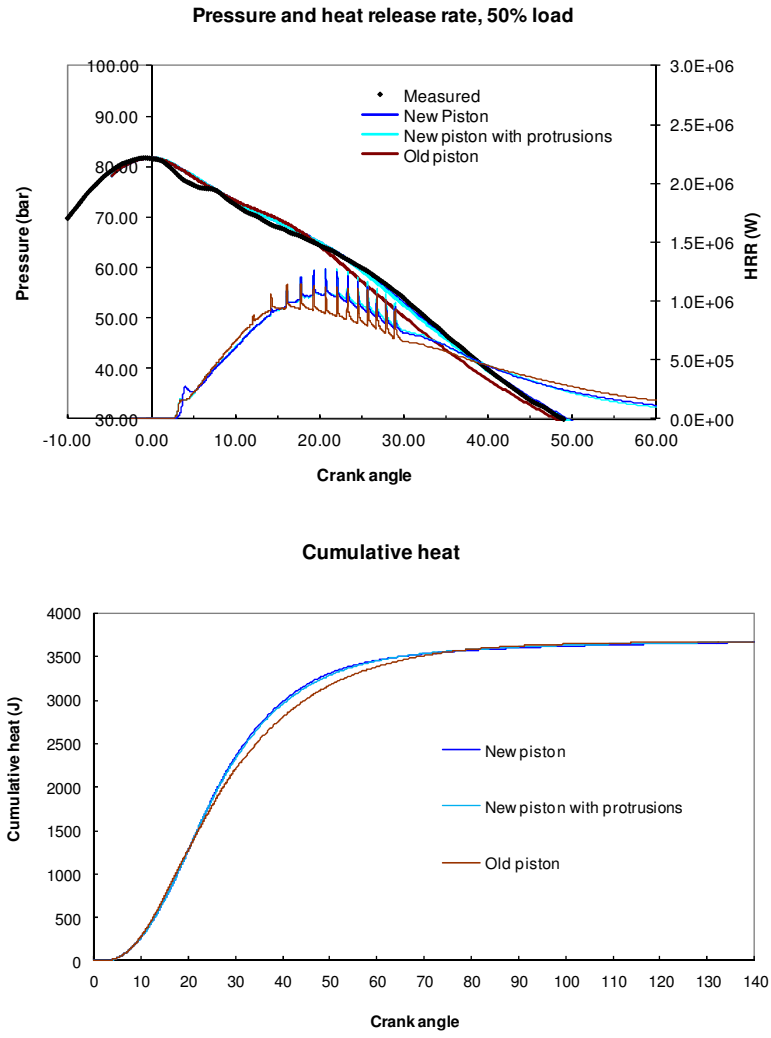


Figure 3.13. Measured and computed cylinder pressure curves together with heat release rates (upper). Computed cumulative heats (lower).

Figure 3.14 shows the soot and NO_x emissions. It is seen that the old piston produces lower NO_x emissions but higher soot emissions. As a whole, the protrusions do not seem to make large contribution to the combustion process. One thing they do is that the flame is mostly taken further away from the cylinder liner compared to the new piston version.

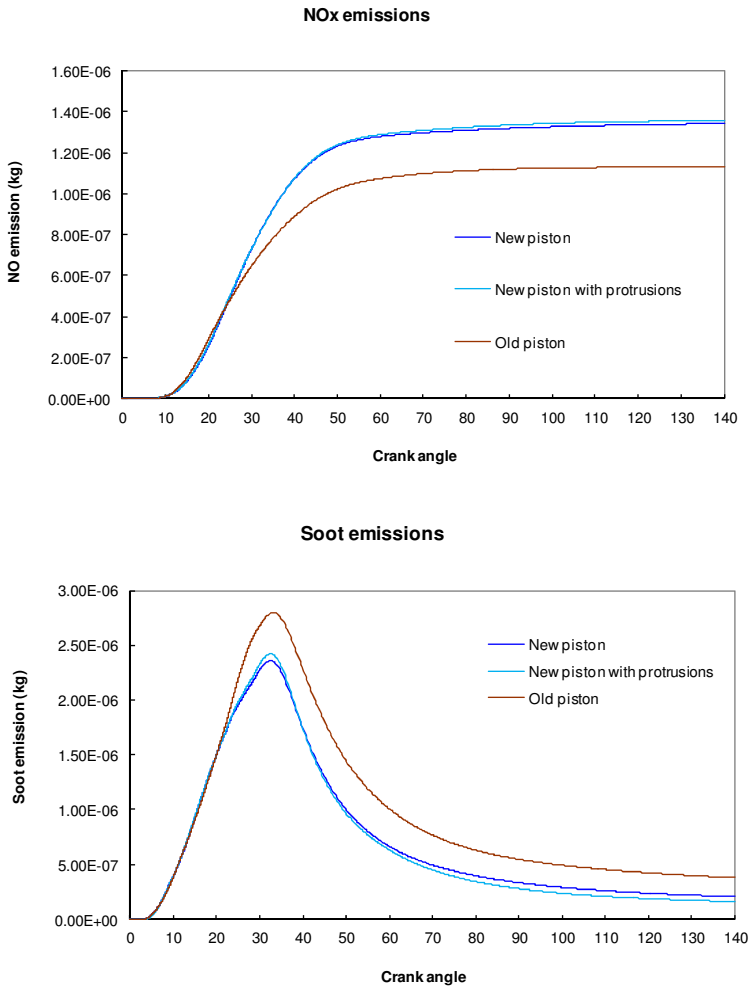


Figure 3.14. Simulated NO_x emissions (upper) and simulated soot emissions (lower).

Comparing the piston top new designs 1, 1.1, and 2

Figure 3.15 shows the measure and calculated pressure and heat release curves as well as the cumulative heats. It is seen that combustion between crank angles 25-45 is enhanced with all the new designs, and increasingly from 1 to 1.1 and to 2. The new piston has lower NO_x emissions than the new designs. The new design 1.1 has the lowest soot emissions. The problem with the new design 2 is that there is relatively strong combustion occurring close to the cylinder liner and that there is some residual fuel left to the piston bowl after the end of combustion. This is why it might have problems

with soot. The new designs 1 and 1.1 have less combustion close to the cylinder liner compared to the new piston.

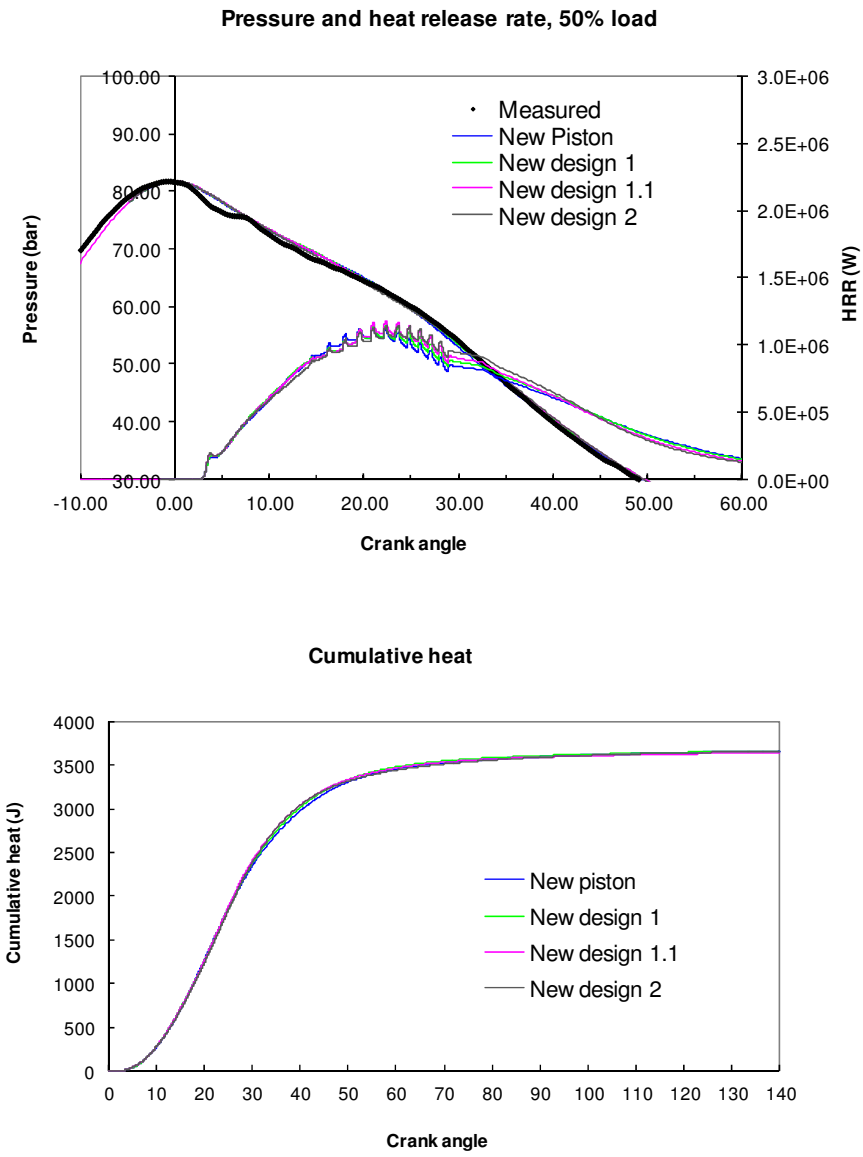


Figure 3.15. Measured and computed cylinder pressure curves together with heat release rates (upper). Computed cumulative heats (lower).

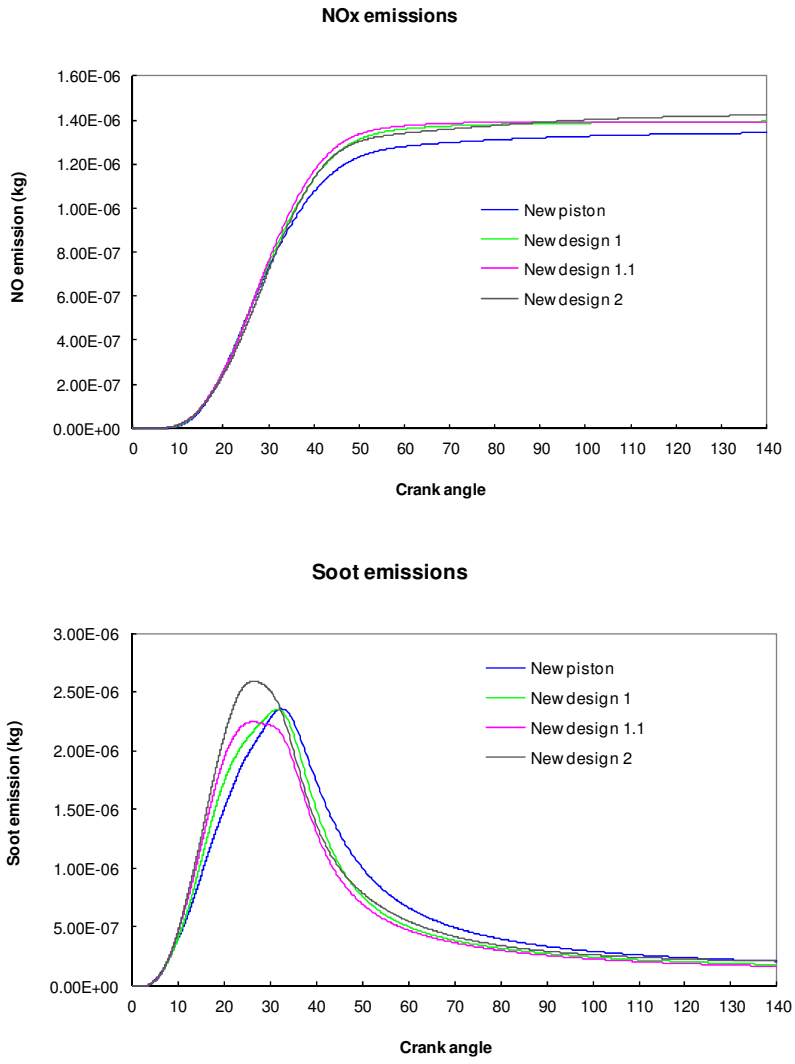


Figure 3.16. Simulated NO_x emissions (left) and simulated soot emissions (right).

3.4.3 Conclusions

Six different piston top shapes were compared with a numerical study. First it can be said that it is difficult to make optimization without proper optimization tools and high amount of simulations. Nevertheless, some useful information was gathered from the optimization process. The currently used piston top shape (new piston) produces more NO_x than the old piston top used by Agco Sisu Power. The opposite is true for soot emissions. The new piston has also higher maximum heat release rate. The

new relatively simple open chamber designs increased the heat release rate between crank angles 25-45. Nevertheless, the total cumulative heat stayed relative constant. The new designs 1 and 1.1 effectively removed the flame from the cylinder liner. It can be concluded that the new designs 1 and 1.1 produce higher mixing rates than the new piston. Higher mixing rates promote higher temperatures which lead to higher NO_x but also to lower soot emissions.

4. Fuel spray measurements (Aalto)

The objective of this experimental study was to compare the global fuel spray characteristics between renewable hydrotreated vegetable oil (HVO) and crude oil based EN 590 diesel fuel. Optical measurements of diesel spray were performed in pressurized test chamber. The spray was non-evaporating. The fuel injection was arranged with a modern common rail fuel injection system and all injection parameters such as injection pressure and time were completely controlled. The fuel spray measurements were made with high speed backlight photography based on short laser pulse and digital image processing. Different injection pressures, orifice diameters, injector types and ambient gas densities were studied. Total 14 different injection parameters were measured. Fundamental spray characteristics were studied, including spray tip penetration, spray angle and velocity of spray tip penetration. Time between electric start and stop of injection and actual start and stop of injection was measured. Under high ambient gas density shock waves was observed and analyzed.

Two different injector types were studied. First injector is typically used at heavy-duty diesel engines in off-road vehicles. This injector was tested with injection pressures 450, 1000 and 1985 bar and orifice diameters 0.08 and 0.12 mm. Ambient density in the test chamber was 36 kg/m^3 that is close to the real engine conditions at the end of compression stroke at 50 % engine load. Another injector is typically used at large scale marine diesel engines. This injector was tested with ambient gas pressures 36 kg/m^3 and extremely high 115 kg/m^3 when injection pressure was 1000 bar and orifice diameter was 0.34 mm.

According to the spray tip penetration measurements, in non-evaporative conditions, no significant and consistent difference were found between crude oil based EN 590 diesel and HVO. Inner delay of injector was shorter with HVO than with EN 590. Hence, there is no need to redesign combustion chamber or readjust injection parameters due to wall impact.

Spray angle was 0.2-2.0 degrees wider when HVO was used with measured injection parameters. Wider spray angle leads to smaller fuel concentration in combustion chamber, assuming that mass flow remain the same as was reported in the earlier studies with GTL fuels. Lower concentration may reduce the soot emissions due to better air-fuel mixing.

Spray tip velocity measurements shows clear difference between HVO and EN 590 diesel fuels. Spray tip velocities are clearly higher with HVO than EN 590 fuel. The maximum velocity was approximately 10-50 m/s higher. However, velocity differences are not high enough to cause significant difference in penetration during the extremely brief monitoring time. Shape of velocity graph is different between different fuels. Velocity difference seems to be especially clear at early stage of spray penetration where velocity maximum was found and velocity maximum seems to stay longer time with HVO than EN 590 diesel fuel. One reason for higher velocity may be the smaller resistance of flow inside of the injector due to physical fuel properties such as viscosity and density or bulk modulus. Shorter inner delays of injectors support the theory that the resistance of flow would be smaller.

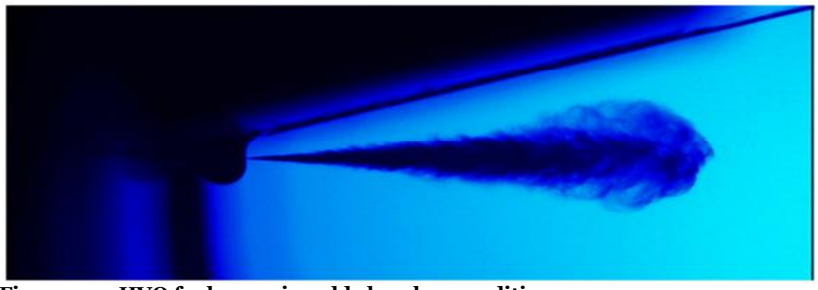


Figure 4.1. HVO fuel spray in cold chamber conditions

5. Medium-speed engine test runs (Aalto)

The engine used in this study is the Extreme Value Engine (EVE). This is a unique medium-speed single-cylinder diesel engine, which is run only for research purposes. The main feature is in the gas exchange valve mechanism: in fact the EVE does not have a traditional camshaft but electro-hydraulic actuators that permit to open and close freely the intake and exhaust valves. Therefore, the gas exchange valve timing is fully controllable and can be adjusted in real-time in order to achieve the best performance at every engine condition.

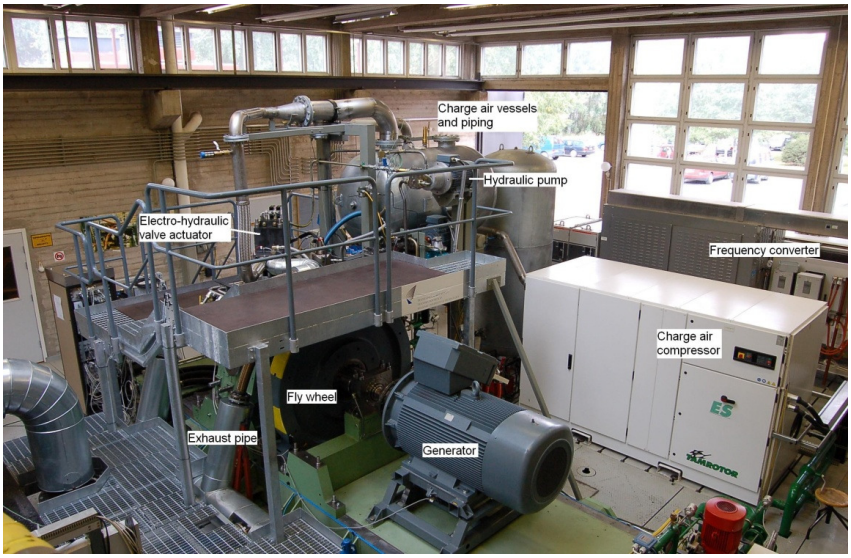


Figure 5.1. EVE engine setup

The renewable fuel used in this work is a hydrotreated vegetable oil (HVO), whose production is based on vegetables oil and animal fats. The fuel used in the runs is the next generation biomass-to-liquids NExBTL, a renewable diesel fuel derived by a patented vegetable oil refining process. This fuel is

composed by isoparaffinic hydrocarbons without aromatic chains as in common diesel fuels. Its chemical composition gives CN is much higher than diesel and the combustion process can therefore be more efficient. Moreover, the linear paraffinic chains avoid the formation of soot, contrarily to what happen with the diesel aromatic rings.

In this study several tests have been performed with HVO to study its behavior in normal operation and in extreme cases. In fact, the conditions in the combustion chamber have been modified changing both the boundary conditions and the valve timing. Using the flexibility of the EVE gas exchange valve system, the compression temperature and the exhaust gas fraction in the charge before the combustion has been modified. The tools considered have been the Miller cycle and the dilution of the charge with exhaust gases.

The Miller cycle has been used to achieve low temperature before combustion and reduce the formation of NO_x. The Miller technique consists of a reduction of the effective compression ratio by changing the closure timing of the intake valve. The Miller cycle has been realized advancing the closing the intake valve before BDC.

Also the exhaust gas fraction in the charge has been changed. Since EVE is not equipped with exhaust gas recirculation (EGR) system, the valve timing has to be opportunely changed to increase the amount of the exhaust residuals in the cylinder, using the so called internal EGR.

The purpose of this work is to study the paraffinic high CN hydrotreated fuel with EVE. Using the high flexibility of the engine, many different gas conditions before combustion have been tested. All the measurements have been taken in steady-state conditions. The intake valve closing (IVC) has been set very early in the intake stroke and its effect, mere and combined with a certain quantity of exhaust residuals has been analyzed. The scavenging phase has been modified by changing the exhaust valve closing (EVC) and the intake valve opening (IVO). The intake valves have been opened both before the EVC (positive scavenging) and after the EVC (negative scavenging). Running with the latter configuration extreme charge conditions at the end of the compression stroke have been reached and at low load the steady-state running is not possible. The most extreme valve timings and the reference one are shown in the figure below (Figure 5.2).

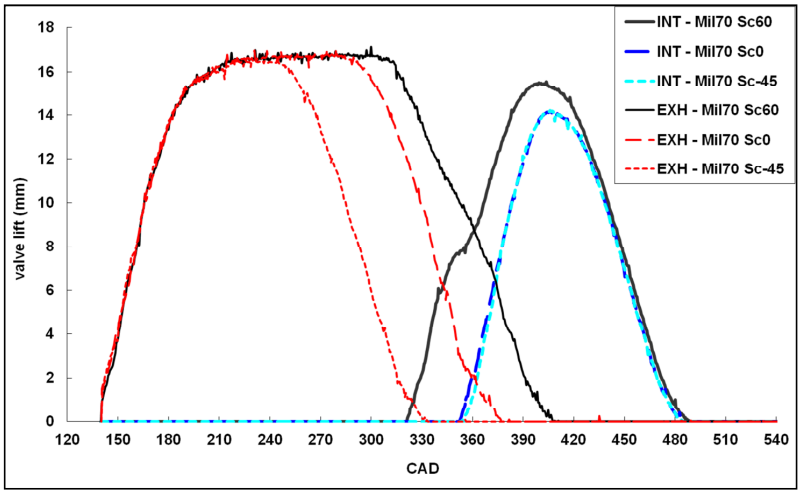


Figure 5.2. Valve timings

The results show that the combustion with HVO improves the engine performance at different loads. In Figure 5.3 the main results are shown. Using the Miller cycle without exhaust gas fraction in the combustion chamber, the NO_x reduction reduces by 40%. Reducing the scavenging phase does not bring further benefits for the performance. Very negative scavenging, instead, increases the fuel consumption.

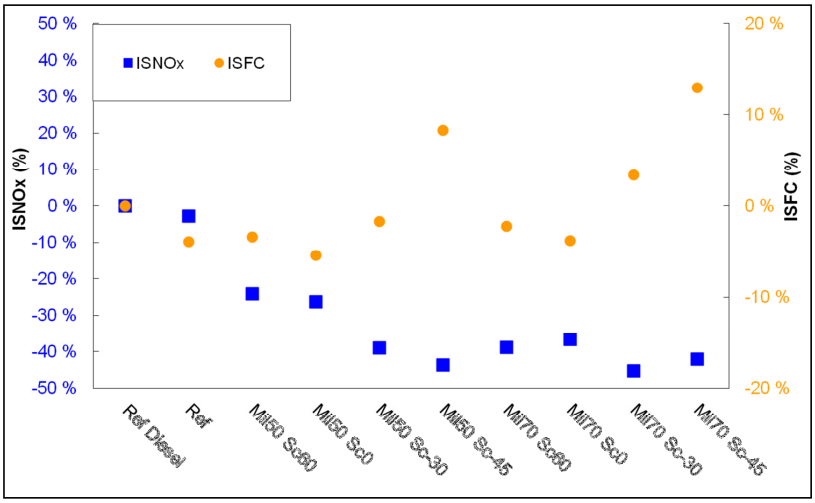


Figure 5.3. Indicated specific NO_x–emission and indicated specific fuel consumption

6. High-speed engine test runs

6.1 Test set-up (AALTO, VTT, TTY)

6.1.1 Engine

The high-speed engine test runs were run using LEO engine (Fig 23) at Aalto University Internal Combustion Engine Laboratory. The engine is a single cylinder common rail diesel heavy duty research engine based on a commercial 6-cylinder Sisu Diesel 84 CTA.

The research cylinder uses the original commercial cylinder head and piston. The five "empty" cylinders have pistons for balancing purposes. Balancing pistons have holes in them so no compression work is done. Basic engine data is shown in Table 6.1. The engine uses an electric motor together with a frequency converter as a dynamometer.

Table 6.1. LEO engine specification

Parameter	Value	Unit
Number of cylinders	1	#
Cylinder diameter	111	mm
Stroke	145	mm
Compression ratio	17:1	

Charge air is supplied by an external air compressor. The system is capable of producing charge air pressures up to 6 bar. Exhaust back pressure can be adjusted using a control valve in the exhaust pipe. The charge air system also has an air heater and a cooler to adjust the charge air temperature. The

mass flow is measured with a Micro Motion coriolis mass flow meter and controlled by a control valve.

Fuel injection parameters, such as injection pressure, injection timing, and injection duration can be adjusted freely. The system is capable of injection pressures up to 1600 bar.

The engine has an electro hydraulic valve actuator system (EHVA) which allows total freedom over gas exchange valve timings and use of different maximum lifts. EHVA makes the engine very well suited for valve timing test runs.

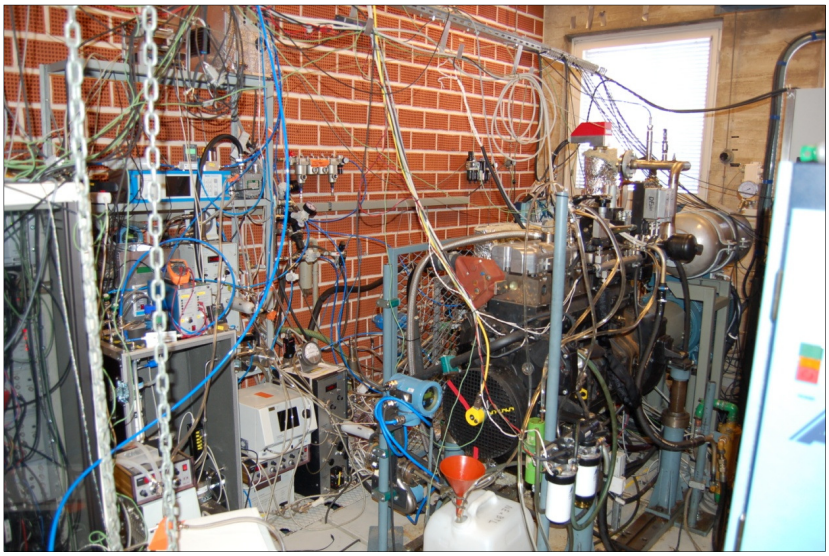


Figure 6.1. LEO engine and some measuring equipment.

6.1.2 Gaseous emission measurements

NO_x emission was measured using Eco Physics CLD 822 S h analyzer.
FTIR analysis was carried out for several gaseous compounds using Gasmet Dx4000N, which is based on Fourier Transform Infra Red (FTIR) – technique. Analyser's sample cell absorption length was 5 meters and temperature 180 °C. The list of analysed compounds is presented in Appendix 3.

Aldehydes were collected from the AVL SPC 472 micro-dilution tunnel using dinitrophenylhydrazine (DNPH) cartridges. The diluted sample gas

was taken from the same location as particulate mass samples. The DNPH derivatives were extracted with acetonitrile/water mixture for analysis with the HPLC-technology (HP 1050/Agilent 1260, UV detector, Nova-Pak C18 column). The list of analysed compounds is presented in Appendix 3.

6.1.3 Particle measurements

Physical properties

- Particle number size distribution was measured using a Scanning Mobile Particle Sizer (SMPS) and an Electrical Low Pressure Impactor (ELPI). With SMPS it is possible to measure particle size distribution in range 10 nm – 460 nm with high accuracy and with time resolution around two minutes. ELPI has time resolution approx. one second, but particle size resolution is somewhat lower. ELPI has measurement range from 7nm to 4um. A Condensation Particle Counter (CPC) is based on optical detection of particles. We had two different CPC models in use (TSI CPC 3775 and 3786), both have lower particle size detection limit around 5 nm. Sampling system consisted of porous tube diluter followed by an ejector diluter. Porous tube diluter enables the formation of nucleation mode similar to real world conditions. Total dilution ratio was around 100. Particle volatility was studied using thermodenuder heated to 265°C.

- The particulate mass emissions (PM) were measured from raw exhaust gas according to ISO8178-2006 standard using the AVL 472 micro-dilution tunnel. Particulate samples were collected on 70 mm teflon coated glass fibre filters (Pallflex TX40HI20-WW). The sample flow through filter was 1.5 g/s and the dilution ratio was 6-7. The filter temperature was kept between 42-52 °C.

- FSN was measured using AVL 415 S variable sampling smoke meter.

Chemical properties (OC/EC, PAH)

- The particulate samples for organic/elemental carbon (OC/EC) analysis were collected using the same device and settings as for PM measurements. The OC/EC samples were collected on 70 mm quartz filters (Munktell MK360)and the thermal-optical analysis of samples was performed with Sunset Laboratories Inc's analyser model 4L using NIOSH 5040 method's temperature profiles.

- For polyaromatic hydrocarbon (PAH) analysis the collected PM samples were extracted with toluene using a Soxhlet method. The extracted soluble organic fraction (SOF) of particle samples were analysed for PAHs using GC/SIM-MS after a liquid chromatographic purification of the extract. The PAH analyses were carried out at Nablabs laboratories. The list of the analysed PAH compounds is presented in Appendix 3.

The measurement setup is presented in Figure 6.2.

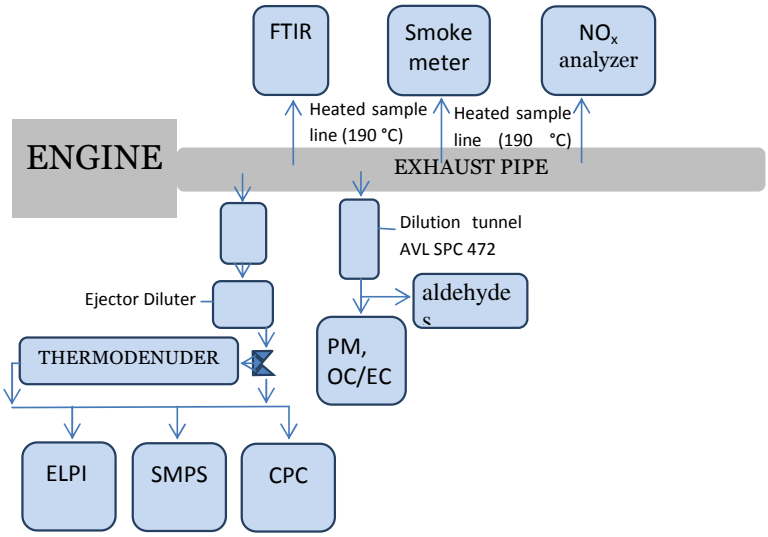


Figure 6.2. Picture covering the whole measurement setup with dilution systems

6.1.4 Test matrix

All tests were run in steady-state conditions with rotational speed of 1500 rpm. The performed test runs were reference tests, EGR tests, miller tests, optimized process test runs with combined EGR and miller, and test runs using oxygenated HVO.

Reference tests

Reference tests were run using both the European standard EN590 diesel fuel and HVO. The original reference points were 25 %, 50 %, 75 %, and 100 % loads. However, in the end the 25 % load case was left out because of problems keeping the charge pressure stable. All the running parameters (injection parameters, charge air pressure and temperature, exhaust back

pressure) were kept as factory standard for a similar commercial engine. Reference points were run with HVO during each individual test run campaign.

EGR tests

EGR tests runs were run at 75 % engine load. The running parameters were kept identical compared with the reference tests and only the EGR percentage was varied. The EGR percentages run were 2.5, 5, 7.5, and 10. The tests were run using HVO.

In the EGR tests neat nitrogen was used as an analog to real exhaust gas. The EGR percentage in this in this report refers to the percentage of added nitrogen (mass) in the charge air. EGR tests were run in October 2010

Miller tests

The miller tests were run at 100 % engine load. Miller timings of 30, 50, and 70 degrees were run. During the miller tests the charge air mass flow was kept same as in the reference points by increasing the charge air pressure (and exhaust back pressure accordingly). The three different timings were run with standard fuel injection and also with an advanced injection timing of 2 degrees.

The degree of miller in this report is the number of degrees earlier the intake valve was closed compared with the standard valve timing used in the reference tests. Miller tests were run in October 2010.

Optimized process

For the optimized process test runs three different running parameters were created for each load point by varying EGR percentage, miller timing and fuel injection parameters. The different points were named LN (Low NO_x), LS (Low smoke), and opt (Optimum). The idea behind the three different points is as follows:

Opt: A good compromise were both NO_x and smoke emission is reduced .

LN: Adjust the parameters to get the minimum of NO_x emission while keeping the smoke emission below the reference emission of EN590

LS: Adjust the parameters to get the minimum of smoke emission while keeping the NO_x emission below the reference emission of EN590

Table 6.2. Running parameters for the optimized process test points

Point	EGR	Miller	Inj. p	SOI var.
50 % Opt	5,0 %	70	600	0
50 % Low NO_x	10,0 %	70	600	0
50 % Low Smoke	2,5 %	70	600	-3
75 % Opt	10,0 %	70	1000	0
75 % Low NO_x	10,0 %	70	1000	2
75 % Low Smoke	2,5 %	70	800	0
100 % Opt	10,0 %	70	1400	0
100 % Low NOx	12,0 %	70	1400	1
100 % Low Smoke	2,5 %	70	1200	0

All tests were run using HVO. Optimized tests were run in February 2011.

Test runs with oxygenated HVO

Due to the low amount of oxygenated HVO available the test matrix was kept quite small. The reference load points of 50, 75, and 100 % were run. Also moderate EGR points of 2.5, and 5 % with 75 % load were run so the results could be compared with the EGR results using neat HVO. Oxygenated HVO test runs were run in May 2011.

6.2 Engine performance (Aalto)

The performance of the engine is evaluated here on indicated specific fuel consumption. The fuel mass flow was measured using a coriolis flow meter and the indicated power for each test was calculated using the cylinder pressure measurements.

6.2.1 Standard operating points (Oct 2010, Feb 2011, May 2011))

Every point was run using standard engine running parameters. Only the fuel was changed. Only very small variation in specific fuel consumption was found between the test fuels. The results are presented in Figure 6.3.

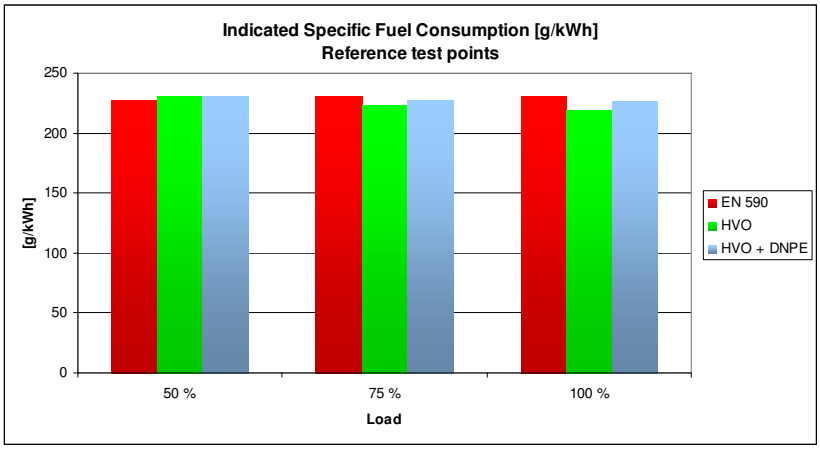


Figure 6.3. Specific fuel consuption with the three different test fuels.

6.2.2 EGR tests (Oct 2010, May 2011)

The EGR percentage was varied while all the other running parameters were kept constant. As the EGR was increased the power of the engine went down and so the SFC went up. 2,5 % and 5 % EGR rate was run with HVO and HVO + DNPE. The results are shown in Figure 6.4.

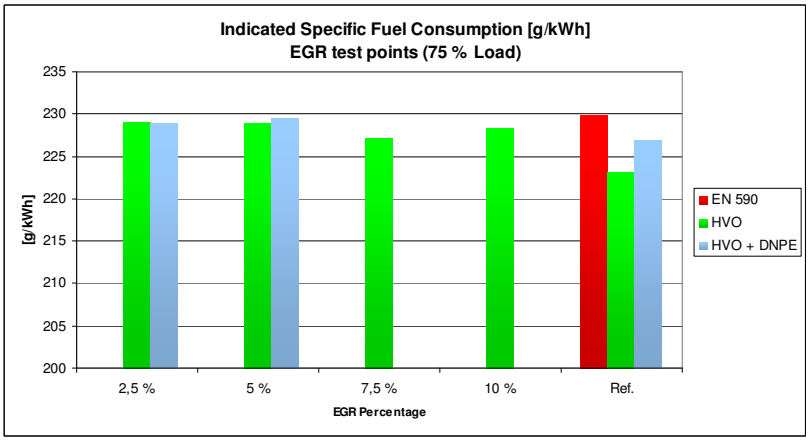


Figure 6.4. Specific Fuel Consumption with varied EGR percentage

6.2.3 Miller tests (Oct 2010)

Three different miller timings were run. The test points were run with standard 2 different injection timings. The charge air mass flow was kept constant which in real engine would mean a different kind of turbo charger. This partly explains the better SFC. The miller tests were run with HVO. The results are shown in Figure 6.5.

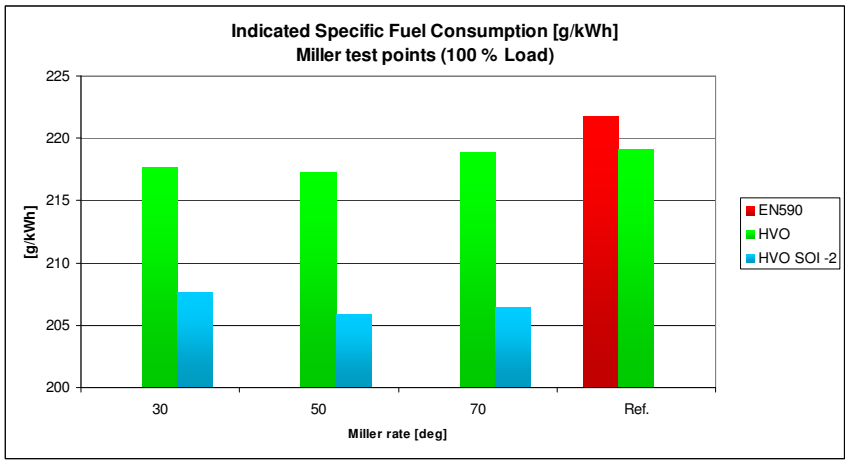


Figure 6.5 Specific fuel consumption with varied miller timing

6.2.4 Optimized process (Feb 2011)

As with the Miller tests the charge air mass flow was kept constant which in real engine would mean a different kind of turbo charger. This partly explains the better SFC. The optimized process tests points were run with HVO. The results are shown in Figure 6.6.

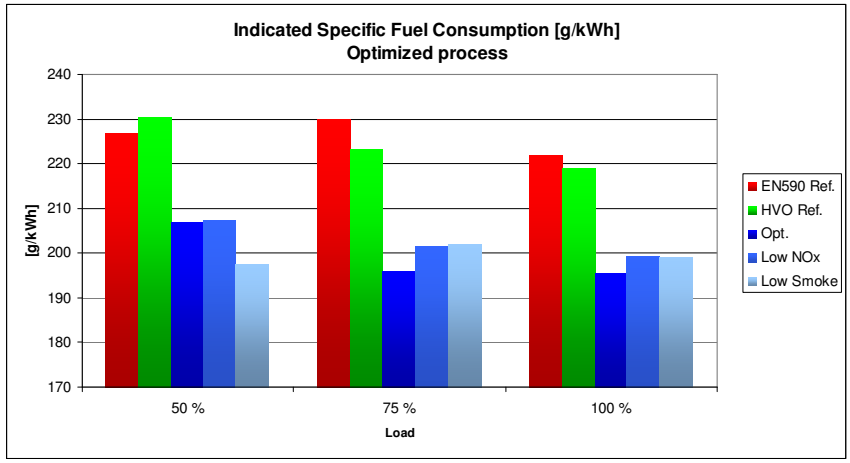


Figure 6.6 Specific fuel consumption in the optimizes process test points.

6.3 Gaseous emissions (Aalto, VTT)

The brake specific NO_x emissions of the reference tests and the separate miller and EGR tests are shown in Figures 6.7 – 6.9. The trend is that with HVO the NO_x emission is slightly lower compared with EN590. The adding of oxygenate to HVO increases the NO_x emission but the emission levels are still lower than with EN590.

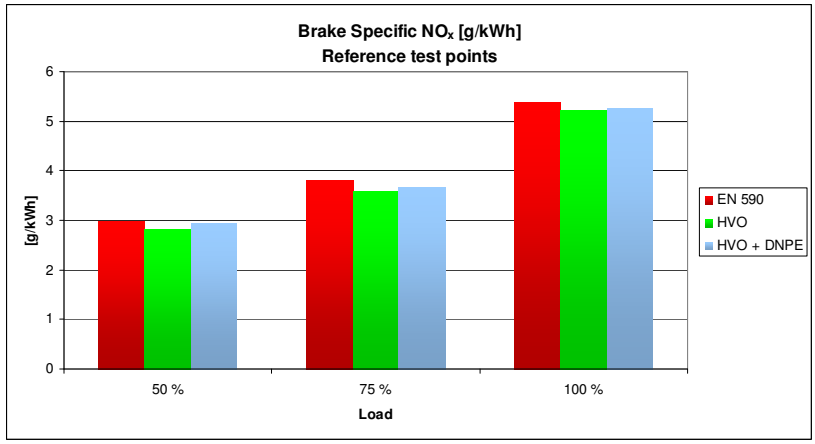


Figure 6.7. Brake Specific NO_x emission at the reference points

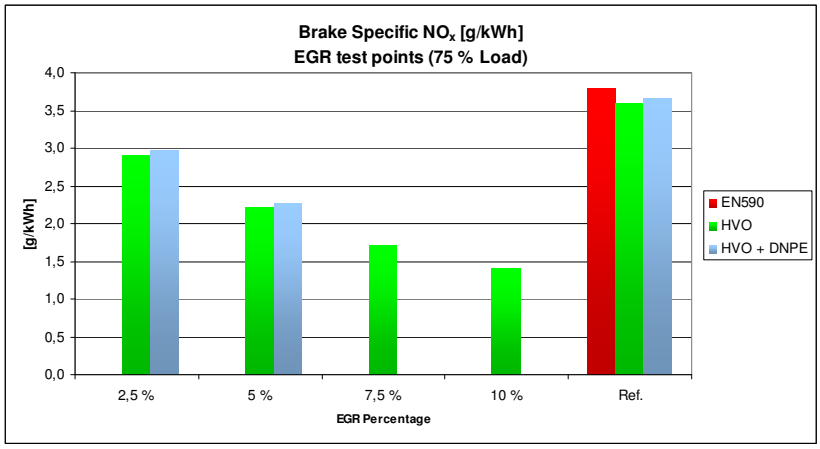


Figure 6.8. Brake Specific NO_x in the EGR test points.

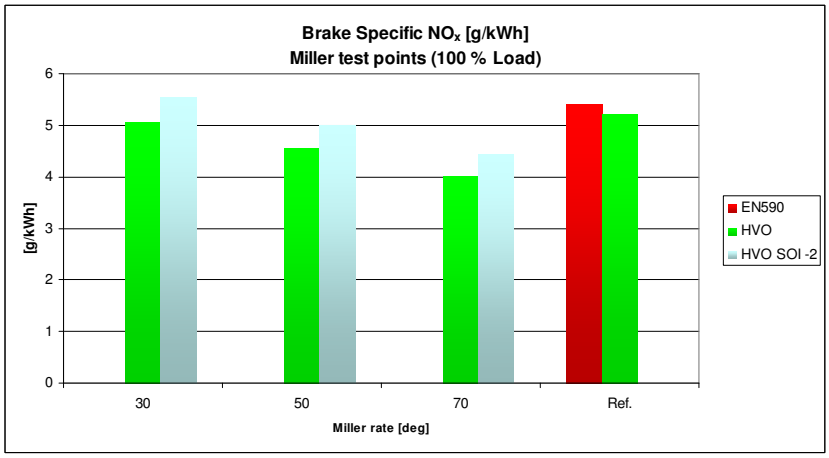


Figure 6.9. Brake Specific NOx in the Miller test points.

In the optimized process tests the NO_x emission is significantly lower in the "Opt" and "Low NO_x" test points. The reduction in the "Opt" test poins was 31-54 % depending on the load. In the "Low NO_x" test points the reduction was 60 – 66 % the biggest reduction being with 100 % load. The results are shown in Figure 6.10.

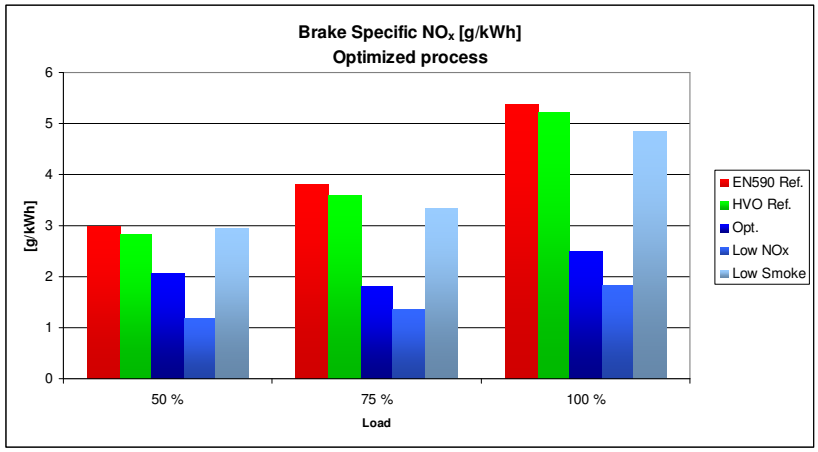


Figure 6.10. Brake Specific NO_x in the Optimized process test points.

6.3.1 FTIR

FTIR was used for monitoring several gaseous compounds. The main purpose was to ensure that untypical engine settings or new type of fuels do not produce any unexpected gaseous emissions. There was no indication of any abnormal emission compounds in the FTIR results. FTIR results were also used as backup information for formaldehyde and acetaldehyde analysis performed by DNPH technique.

6.3.2 Aldehydes

The dominating aldehyde compounds in diesel exhaust are form- and acetaldehyde and therefore this report concentrates to these two compounds.

The reproducibility of formaldehyde emissions is presented in Figure 6.11. Primarily the aldehyde emissions were analysed using DNPH cartridge technique. When a change in aldehyde emissions levels between 2010 and 2011 was noticed, the formaldehyde was analysed also from the FTIR data. This was done to see if both analysis methods show similar trends. When comparing formaldehyde emissions in 75 and 100% loads, there is a clear increase in 2011 results. At 50% load the level of formaldehyde has not changed significantly. These trends were also noticed for acetaldehyde. Due to change on aldehyde emissions the comparison of results is divided between 2010 and 2011.

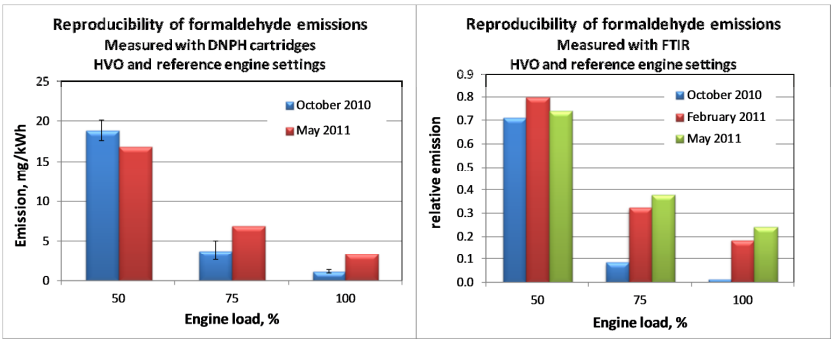


Figure 6.11, Reproducibility of formaldehyde emissions.

In October 2010 the EN590 and HVO were measured with reference engine settings. The results are presented in Figure 6.12. At 75 and 100% loads the form- and acetaldehyde emissions are very low and there is no difference between fuels. With 50% load the form- and acetaldehyde emissions decreased by 20% with HVO.

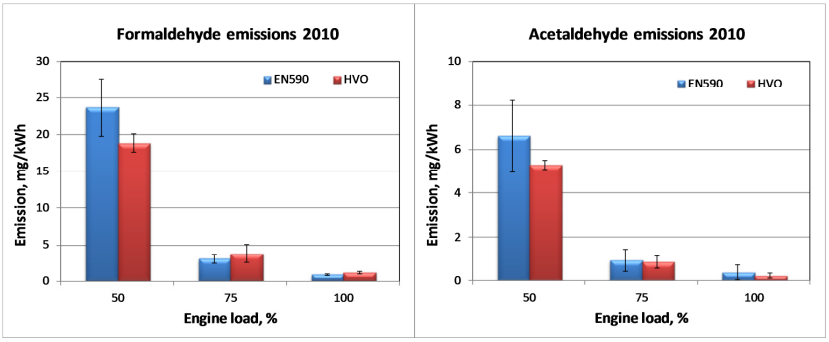


Figure 6.12, Form- and acetaldehyde emissions with EN590 and HVO. Measured in 2010.

The Figure 6.13 presents the aldehyde emissions measured with HVO and HVO+DNPE fuels in 2011. The form- and acetaldehyde emissions are slightly lower with HVO+DNPE compared to HVO on 50% engine load. On 75 and 100% loads there is an increase in aldehyde emissions with HVO+DNPE fuel. These trends are supported by FTIR data. However, the aldehyde emissions are very low on high engine loads therefore the changes on aldehyde emissions are not very significant.

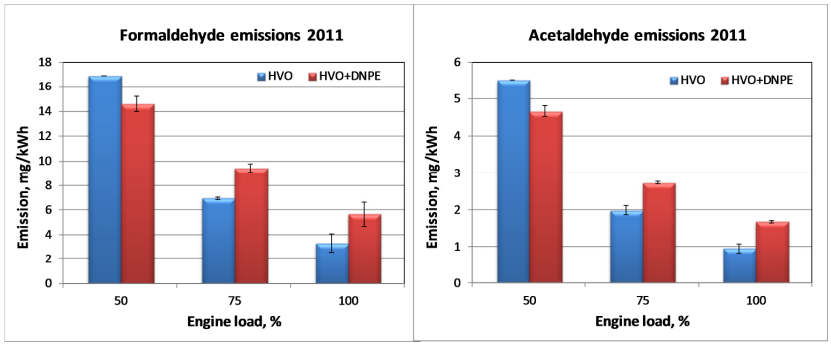


Figure 6.13, Form- and acetaldehyde emissions with HVO and HVO+DNPE. Measured in 2011.

The comparison of aldehyde emissions with HVO using reference and optimised engine settings are presented in Figure 6.14. On 100% load the formaldehyde emission increase significantly with optimised engine settings. The similar increase is seen also with acetaldehyde but since acetaldehyde emission level is very low, the importance of the increase is not very significant. On 50% engine load the aldehyde emissions decrease with optimised engine settings and on 75% load the emissions are basically the same with both engine settings.

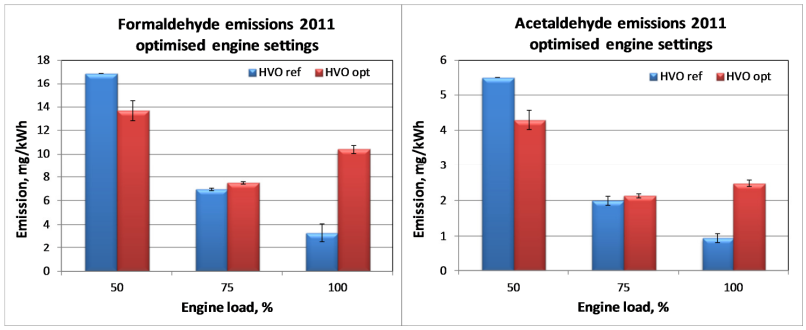


Figure 6.14, Form- and acetaldehyde emissions with reference and optimised engine settings. Measured in 2011.

6.4 Particle emissions (TTY, VTT)

6.4.1 Reproducibility of particle emissions

Particle emissions were performed at three different measurement campaigns: October 2010, February 2011 and May 2011. In all measurement campaigns, particle emission consisted of a single mode (soot mode) having geometric mean diameter (GMD) around 60 nm at standard conditions.

In Figure 6.15 the reproducibility of PM measurements at different measurement campaigns for the reference conditions with HVO fuels on studied loads is presented. It can be concluded that PM measurements of reference conditions agree well between different measurement campaigns.

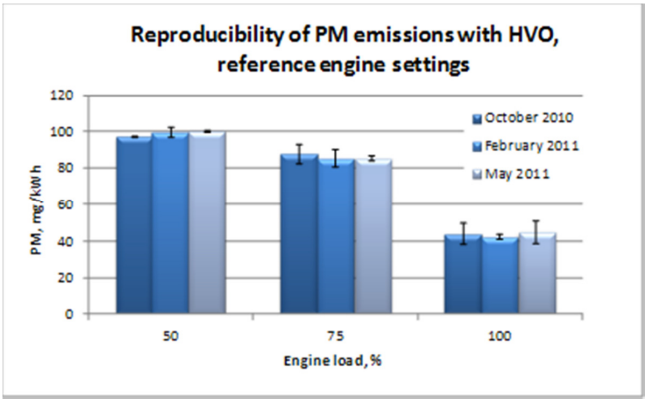


Figure 6.15. Reproducibility of PM emissions with HVO at reference engine settings on studied loads

In Figure 6.16 similar comparison is carried out for the geometric mean diameter of the soot mode. It can be seen that only small variance in particle size is present between the studied loads at reference conditions. The 75 % load produces largest particle mode (GMD roughly 65 nm). On 50 % and 100 % loads the GMD is around 60 nm. It can be also seen that although 50 % and 75 % loads are quite reproducible in terms of GMD, more variance in GMD exists at 100 %. However, it should be noted that the differences in GMD are overall quite small and, thus, have no significant effect on total particle mass. Thus, particle size measurements are in line with PM measurements in terms of reproducibility.

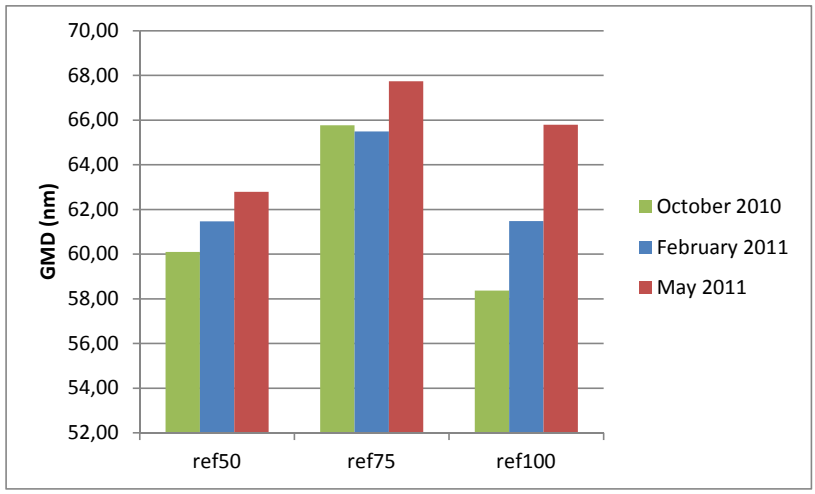


Figure 6.16. Reproducibility of geometric mean diameter measurements in different campaigns with HVO

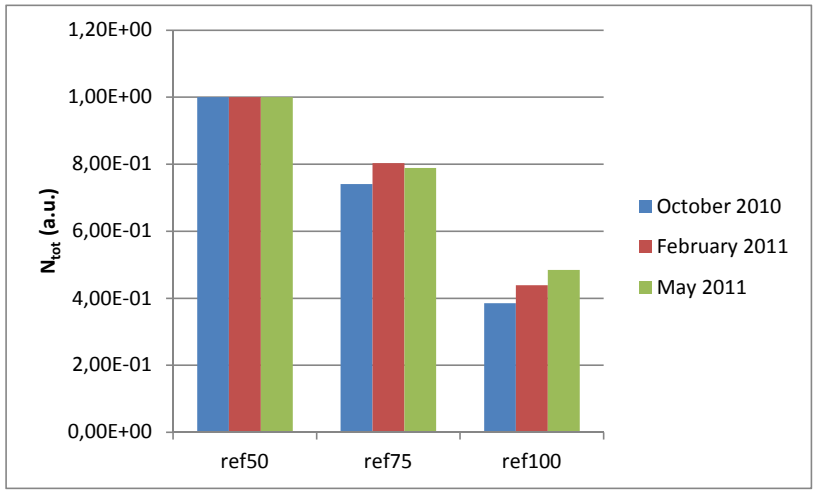


Figure 6.17. Reproducibility of particle concentration changes at reference conditions with HVO

Particle number emission was measured slightly differently in all three measurement campaigns. Thus, direct comparison of absolute values between different campaigns is not sensible. However, relative changes in particle concentration are quite reproducible as it can be seen from Figure 6.17. In the figure, the particle concentration is normalized to unity on 50 % load at reference conditions (with HVO) for each measurement campaign.

6.4.2 Particle emissions with different fuels

Particle emissions were measured with three fuels: with fossil EN590, with HVO and with HVO where 20 % DNPE was added. The measurements were performed using reference engine conditions. The results are presented in Figures 6.18 and 6.19. In Figure 6.18, PM measurements are shown with different fuels. The HVO results are averages of October 2010 and May 2011 results. It can be seen from the figure that HVO decreases PM emissions over 30 % relative to fossil EN590 whereas HVO + 20% DNPE decreases PM emissions roughly 50 % with all studied loads.

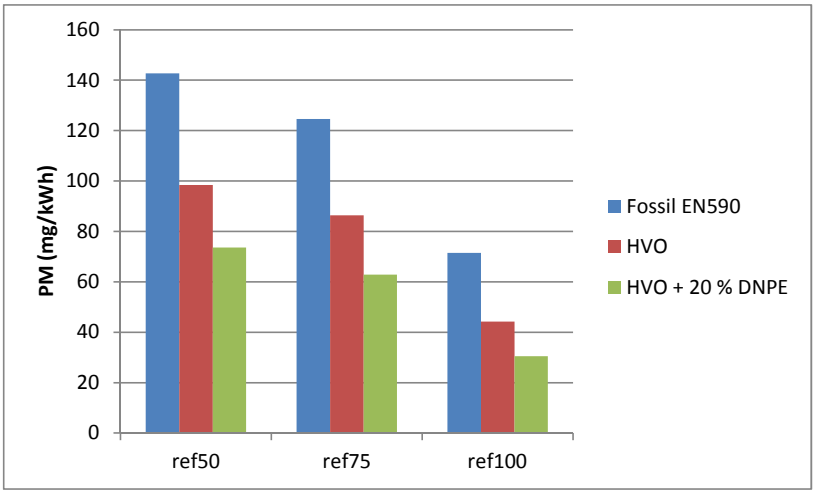


Figure 6.18. PM emissions with the studied fuels.

The decrease in particle emissions relative to fossil EN590 can be seen also in particle number emissions. In Figure 6.19, the relative changes in particle number emissions are presented. The particle number emission of HVO on 50 % load at reference conditions is normalized to one. With HVO, the relative changes in particle number between different loads are averages of October 2010 and May 2011 results. The results in Figure 41 show that particle number reductions are at their greatest on 50 % load reaching almost a 20 % decrease when changing from EN590 to HVO and almost a 30 % decrease when changing to oxygenated HVO. On higher loads the number emission decreases were somewhat smaller being roughly 12 % when changing to HVO and 20 % when changing to oxygenated HVO.

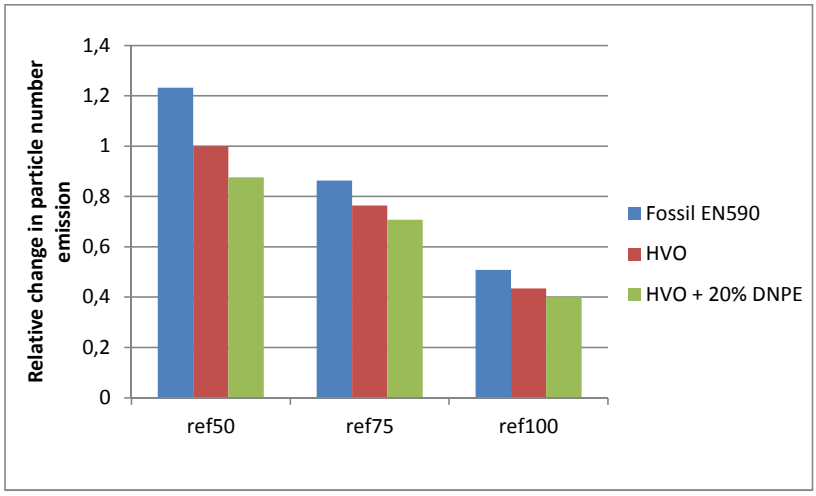


Figure 6.19. Relative changes in particle number emission due to fuel change with the studied engine conditions. The changes are normalized to 50 % load reference conditions with HVO fuel.

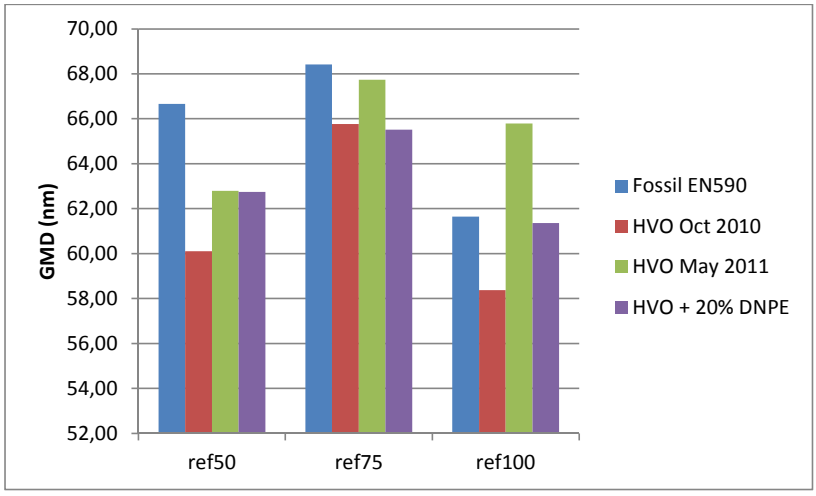


Figure 6.20. Geometric mean diameters (GMD) of soot particles measured with different fuels

In Figure 6.20, the geometric mean diameters measured using different fuels are presented. The figure shows that GMD remained quite unchanged although the fuel was changed.

For a more detailed study on the effects of HVO+oxygenate blend to exhaust emissions, see Happonen et al. 3/2012 (Fuel, reference 10).

6.4.3 Engine optimization results

In order to see the effect of changes in engine parameters to different emissions is, it is first sensible to study the emissions at the standard conditions for each load. These emissions are presented in Table 6.3. Each standard condition was measured at two separate times. Each measurement time included one PM measurement and two to three particle size distributions from which total particle number (N_{tot}) and geometric mean diameter (GMD) were obtained. ,

Table 6.3. Particulate matter (PM), total particle concentration (N_{tot}) and geometric mean diameter of the particle size distribution (GMD) of the engine at 50, 75 and 100 % loads with studied engine conditions.

	Load (%)	PM (mg/kWh)	N_{tot} *1e15 (#/kWh)	GMD (nm)
ref	50	99	1.28	61.5
	75	85	1.03	65.5
	100	42	0.56	61.5
Opt	50	74	1.38	55.3
	75	56	1.05	55.2
	100	28	0.46	52.7
LN	50	169	2.61	66.6
	75	103	1.62	62.7
	100	49	0.76	57.9
LP	50	52	0.77	50.6
	75	32	0.50	51.5
	100	13	0.14	49.7

The results of the optimization campaign regarding particulate emissions are presented in Figure 6.21. In the figure, the changes caused by optimizing the engine to different conditions are shown. The changes are relative to the reference conditions on the given load with HVO fuel.

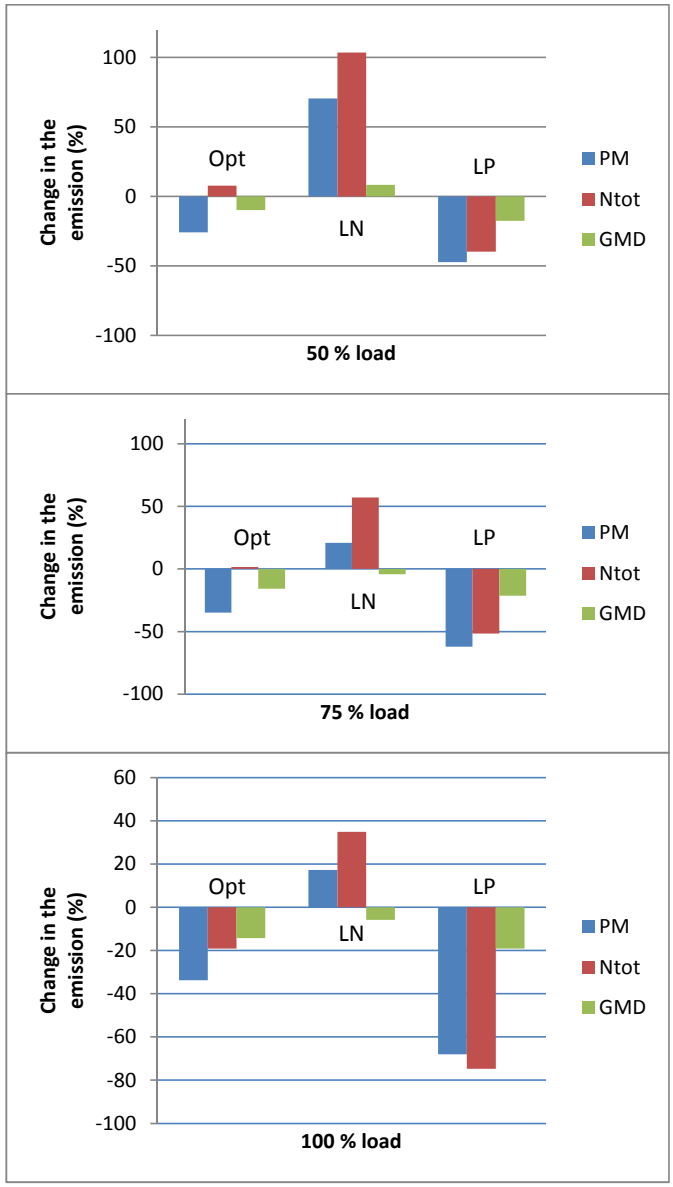


Figure6.21. Relative changes in particulate (PM, number concentration and GMD) emissions due to engine optimization at the studied engine loads.

With the low- NO_x (LN) conditions, the increase in PM emission is at maximum on 50 % load being as much as 70 %. This is approximately 17 % greater than the emission with fossil EN590 fuel at the standard engine conditions in the previous campaign. On other loads at LN conditions, the soot PM emission was greater than at the standard engine conditions with HVO fuel but (over 15 %) lower than at the standard conditions with EN590 fuel. As it can be seen from Figure 6.21, at 75 % and 100 % loads, the

geometric mean diameter (GMD) of the soot particle distribution actually decreases somewhat at LN conditions although PM increases. Thus, particle number concentration (Ntot) is increased (15 – 30 % units) more than PM relative to the standard conditions. This is also the case on 50 % load where there is a small increase in particle size.

At low-smoke conditions (LP), PM emission was decreased 45 – 68 % at depending on load. The reduction in particle number concentration was quite near the reduction in PM emission on all loads. However, the GMD of the distribution decreased roughly 20 % on all loads.

The optimum conditions were chosen to show how much both of these emissions can be reduced together. The results show that soot PM emission decrease 25 – 33 % depending on load. With all loads, optimum conditions decrease the GMD of the particle size distribution over 10 %. Particle number emission either remains on the reference level (on 50 % and 75 % load) or is decreased somewhat (on 100 % load). Thus, the main reason in lowering PM at optimum conditions on 50 % and 75 % loads is the decrease in particle size.

A more detailed discussion of the optimization results can be found in Happonen et al. 2/2012 (Fuel, reference 9).

6.4.4 EGR and Miller results (TUT)

Table 6.4 shows particle number, PM and NO_x – emissions with different fuel blends, engine and EGR settings.

Advancing SOI by 70 °CA lowered NO_x emission from 5.20 g/kWh to 4.01 g/kWh with the HVO fuel, but at the same time PM emission increased to the same level with the EN590 fuel and standard engine settings. Miller test lowered the cylinder peak temperature and pressure, therefore reduced NO_x -formation.

When Miller was combined with ASOI (respectively by 70 °CA and 2 °CA), the PM emission dropped to 36 mg/kWh and NO_x emission to 4.44 g/kWh. The engine used in this study had standard SOI timing set to quite late (ASOI 1.6 °CA) to achieve low NO_x emission. Miller combined with ASOI 2°CA reduced specific fuel consumption (SFC) around 4.5% and Miller 70 with ASOI 3 reduced SFC by 7.3% compared to standard SOI timing.

DNPE blending decreased particle number emission 10.2-17.5% depending on load point, PM was reduced 26-33%. DNPE blending combined with EGR increased particle number emission 28-114% while NO_x decreased 23-38 %.

The effect of Miller timing has been discussed also in Heikkilä et al (2012, reference 12).

Table 6.4. Particle number and PM with different combination of fuel, engine and EGR settings.

	Load	Particles	PM	NOx	Campaign
Fuel / meas. Point	%	#/kWh	mg/kWh	g/kWh	
EN590 / ref50	50	1.3E+16	143	2.98	10/2010
EN590 / ref75	75	8.9E+15	125	3.80	10/2010
EN590 / ref100	100	5.2E+15	71	5.39	10/2010
HVO / ref50	50	1.0E+16	97	2.83	10/2010
HVO / ref75	75	7.6E+15	88	3.59	10/2010
HVO / ref100	100	4.0E+15	44	5.20	10/2010
HVO / EGR 2.5	75	1.1E+16		2.91	10/2010
HVO / EGR 5	75	1.6E+16	223	2.20	10/2010
HVO / EGR 7.5	75	2.3E+16		1.71	10/2010
HVO / EGR 10	75	3.1E+16		1.41	10/2010
HVO / Miller 30	100	4.3E+15		5.07	10/2010
HVO / Miller 50	100	5.3E+15		4.54	10/2010
HVO / Miller 70	100	7.2E+15	72	4.01	10/2010
HVO / Miller 30, ASOI 2	100	2.2E+15		5.54	10/2010
HVO / Miller 50, ASOI 2	100	2.4E+15		4.99	10/2010
HVO / Miller 70, ASOI 2	100	3.3E+15	36	4.44	10/2010
HVO / Miller 70, ASOI 3, EGR 2.5	100	4.6E+15		3.73	10/2010
HVO / ref50	50	2.98E+14	100	3.0	5/2011
HVO / ref75	75	2.35E+14	85	3.6	5/2011
HVO / ref100	100	1.45E+14	45	5.0	5/2011
HVO / EGR 2.5	75	3.50E+14	132	2.9	5/2011
HVO / EGR 5.0	75	5.95E+14	236	2.2	5/2011
HVO+DNPE / ref50	50	2.61E+14	74	2.9	5/2011
HVO+DNPE / ref75	75	2.11E+14	63	3.7	5/2011
HVO+DNPE / ref100	100	1.20E+14	30	5.3	5/2011
HVO+DNPE / EGR 5.0	75	5.05E+14	145	2.3	5/2011
HVO+DNPE / EGR 2.5	75	3.02E+14	86	3.0	5/2011

6.4.5 Chemical analysis of particles (VTT, TUT)

Generally little or no observed difference in particle diameter was found between particles treated with a thermodenuder and particles that bypassed the thermodenuder. The result indicates that the amount of semivolatile matter on the surface of exhaust particles was quite low.

A measurement device called hygroscopic tandem differential mobility analyzer was tested during the oxygenate measurement campaign. The device measured hygroscopicity, i.e. the ability of particles to grow due to water The results indicate that there is no significant difference between the hygroscopicity of HVO and fossil diesel generated particles. That is, the particles emitted from the engine should behave similarly in the atmosphere regardless of the studied fuel. More information of the hygroscopicity of the particles as well as more detailed discussion of the oxygenate results can be found in Happonen et al. 3/2012 (Fuel, reference 10).

The particulate samples were analysed for organic and elemental carbon and for PAH content. The PAH analysis was performed from the soluble organic fraction (SOF) of samples.

OC/EC

In Figure 6.22 the reproducibility of OC/EC analysis is presented. The results in 2010 and 2011 are consistent.

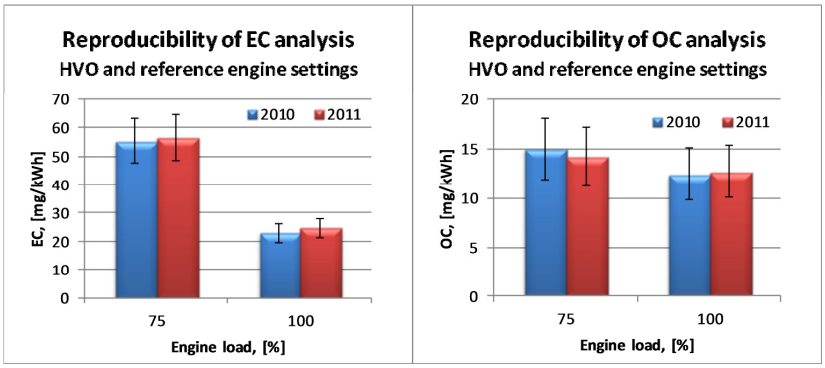


Figure 6.22. Reproducibility of OC/EC analysis, HVO fuel and reference engine settings.

The relative OC/EC-emissions of PM samples with different fuels and engine loads are presented in Figure 6.23. The total carbon (TC) emission with EN590 fuel and 75% engine load is the reference against which other results have been compared. TC is the sum of EC and OC. The HVO and HVO+DNPE fuels decrease the total carbon emission significantly compared to EN590 diesel. The difference is mainly caused by the decrease of elemental carbon. The amount of organic carbon decreases as well but not as much as the amount of EC.

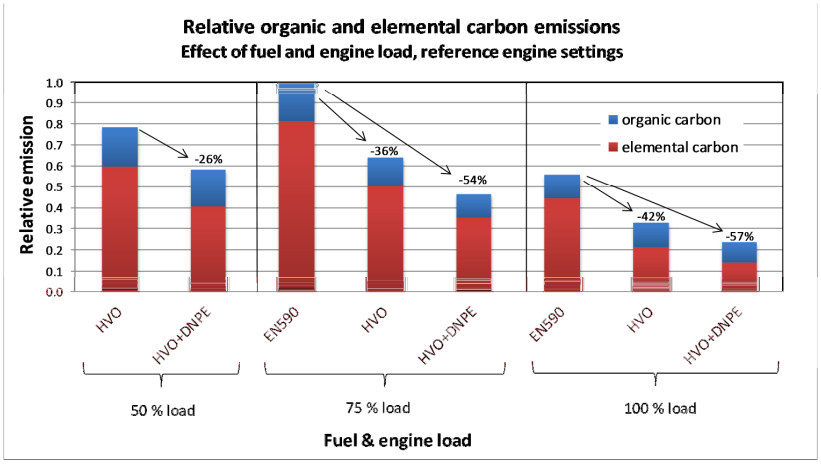


Figure 6.23, Organic and elemental carbon emissions with different fuels and engine loads.

Figure 6.24 presents the carbon emissions with different engine settings and loads with HVO fuel. The results are compared to TC emissions with reference engine setting on 50% load. With each load the LP settings produce the lowest TC emission and with the LN settings the TC emission are the highest. The different engine settings affect to both, EC and OC. Yet again the change in EC is more significant compared to changes in OC.

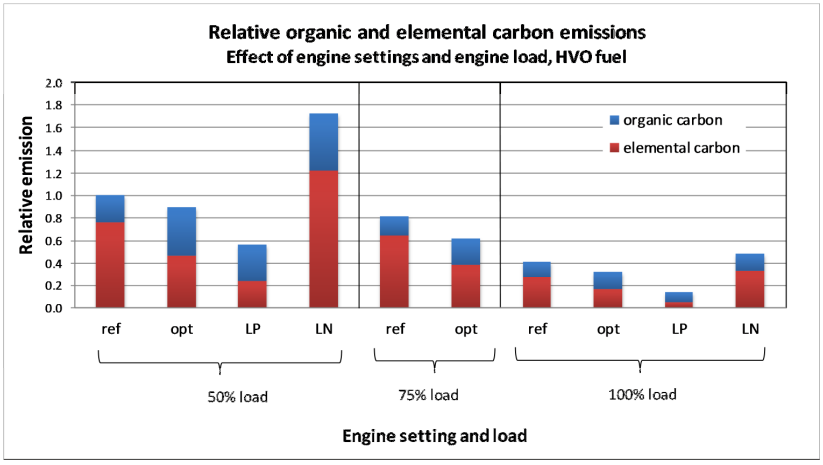


Figure 6.24, Organic and elemental carbon emissions with different loads and engine settings.

In Figure 6.25 the OC/EC results with different EGR settings and different fuels are compared against reference engine settings with HVO and 75%

engine load. Using EGR increases significantly the EC emissions but the OC emissions are increased only slightly. With both fuels the changes are similar.

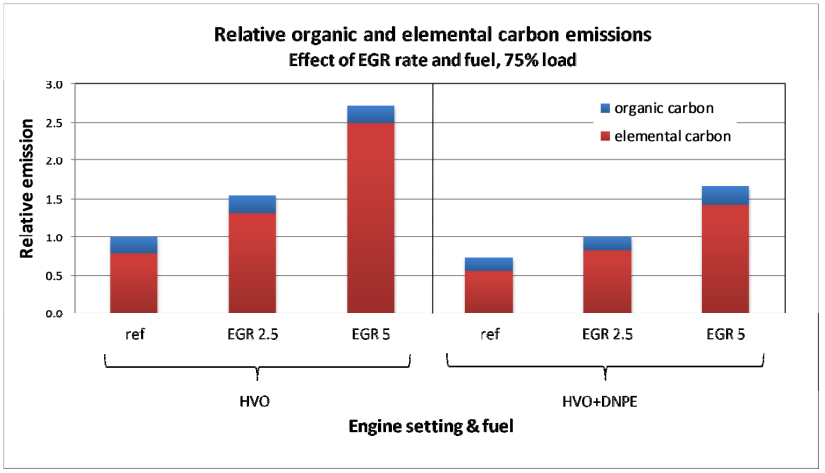


Figure 6.25, Organic and elemental carbon emissions with different fuels and EGR settings, 75% engine load.

PAH emissions

There are several lists on priority PAHs. In this report, the sum of seven and fourteen PAH compounds are reported based on the European and the US EPA definitions.

The reproducibility of PAH analysis is presented in Figure 6.26. The deviation of results rather high and there is some differences in result measured on 2010 and 2011. Nevertheless, the differences of results are not that high that it would prevent the comparison between the measurement periods.

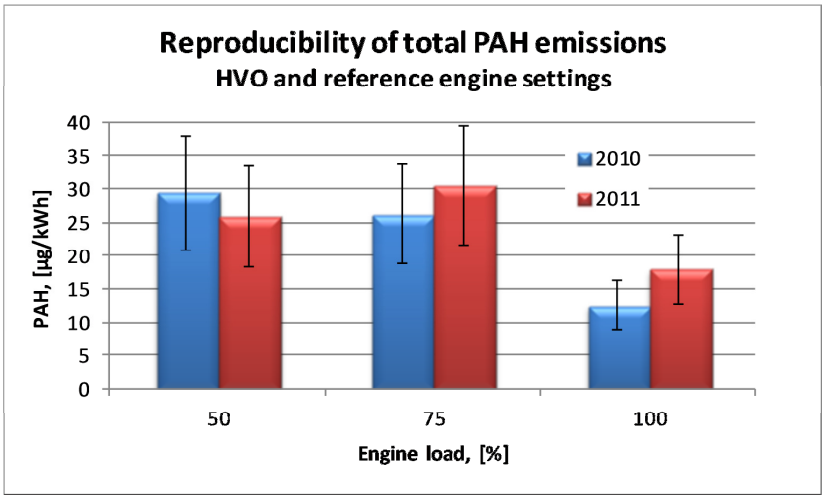


Figure 6.26. Reproducibility of PAH analysis with HVO fuel and reference engine settings.

The results are presented as total PAH, PAH14 and PAH7. The total PAH emissions include all the analysed PAH compounds and PAH14 and PAH7 are two different listings of the most harmful PAH compounds. As Figure 6.27 shows, changing the EN590 diesel to HVO or HVO+DNPE fuel decreases total PAH and PAH 14 emissions. The amount of PAH7 compounds is insignificant with each fuel. With HVO+DNPE the PAH14 emissions were decreased by 74 and 62% on 50 and 75% loads compared to EN590. With HVO the PAH14 emissions were from 42 to 55% lower in comparison with EN590.

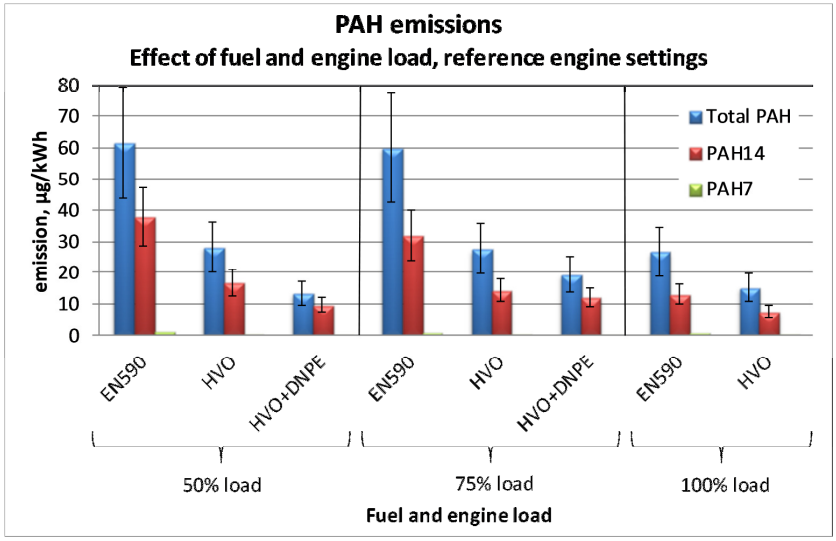


Figure 6.27, PAH emissions with different fuels and engine loads.

Figure 6.28 presents how optimised engine settings affect to PAH emissions with HVO. The PAH14 emissions were reduced by 56-70% with optimised engine settings. The total PAH emission were reduced even more.

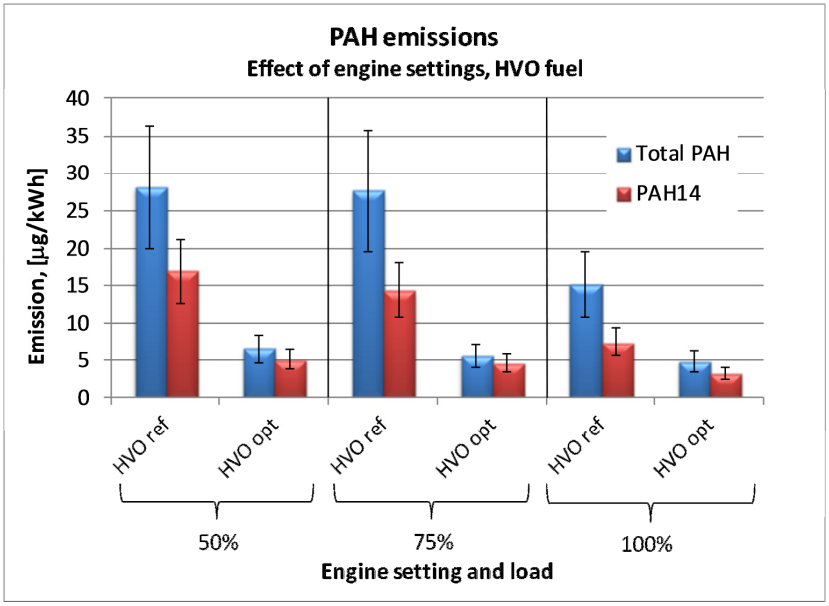


Figure 6.28, PAH emissions with different loads and engine settings.

7. Summary

The objective of this study is to develop new extremely low emission combustion technologies for renewable fuels in compression ignition engines. The target is to cut down emissions at least by 70%. The scope is to utilize the physical and chemical properties of the renewable fuels that differ from properties of the traditional crude oil based fuels and to develop optimum combustion technologies for them.

7.1 Fuels

The novel paraffinic diesel fuels have excellent physical and chemical properties. Renewable diesel fuel, HVO, is an example of paraffinic high-cetane, low-aromatic diesel fuel. Paraffinic HVO does not suffer from storage and low temperature problems. The combustion related properties of paraffinic fuels are excellent enabling engine operation with reduced nitrogen oxide emission without suffering from traditional trade-off with increased particle matter emission.

Combination of paraffinic fuel and an oxygenated diesel component could offer further benefits in engine performance and exhaust emissions. A large number of oxygenates were reviewed to find the most promising candidate in this respect. Di-pentyl ether (DNPE) was selected for the tests due to its diesel-like fuel properties and low exhaust emissions reported in literature. Paraffinic HVO as such and with oxygenate were used in this study in comparison with conventional diesel fuel.

7.2 Combustion analysis

The optimization of piston top shape revealed a new design that reduced the soot emissions compared to the currently used piston shape. Concerning Phi-T maps, it can be concluded that NO_x emissions can be well predicted by looking at Phi-T map data only but soot emissions are more difficult as the maps do not take mixing into account.

7.3 Fuel spray measurements

No significant and consistent difference was found in the spray tip penetrations between crude oil based EN 590 diesel and HVO in the fuel spray chamber tests. Hence, there is no need to redesign combustion chamber or readjust injection parameters due to wall impact. Spray angle was 0.2-2.0 degrees wider when HVO was used with measured injection parameters, which means lower local fuel concentration and so lower soot emissions.

Spray tip velocity measurements shows clear difference between HVO and EN 590 diesel fuels. Spray tip velocities are clearly higher with HVO than EN 590 fuel. The maximum velocity was approximately 10-50 m/s higher. However, velocity differences are not high enough to cause significant difference in penetration. One reason for higher velocity may be the smaller resistance of flow inside of the injector due to physical fuel properties such as viscosity and density or bulk modulus.

7.4 High-speed engine tests

In the high speed engine tests the goal of 70 % reduction in NO_x emission with PM emisison no higher than the reference and vice versa was achieved or very nearly achieved depending on the load point. Generally it can be said that particle matter emission can be affected or even controlled significantly with the HVO-fuels and engine settings used in this study.

Compared with EN590 the use of HVO and HVO+oxygenate decreases greatly the PM emissions by significant reduction of elemental carbon. There is also a small decrease in organic carbon emission. PAH, emissions decreased as well. Aldehyde emissions were lower at 50% load but slightly

higher or the same on high engine loads. When comparing HVO with HVO+oxygenate it was found the oxygenated fuel had smaller PM and PAH emissions but higher aldehyde emissions on high loads.

When comparing HVO with HVO+oxygenate it was found the oxygenated fuel had smaller PM emission but slightly higher aldehyde emission, both being substantially lower than the emissions when using EN590. All in all, the relative decrease in particulate emissions caused by changing the fuel from HVO to HVO-oxygenate blend was of the same order of magnitude than the decrease caused by changing the fuel from fossil EN590 to HVO fuel.

7.5 Medium-speed engine tests

The results of the medium-speed engine tests showed similar effects on smoke and NO_x emissions as the high-speed engine tests.

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3. Gong Y, Kaario O, Tilli A, Larmi M, and Tanner F. A computational investigation of hydrotreated vegetable oil sprays using RANS and a modified version of the RNG k-epsilon model in OpenFOAM, SAE Technical Paper Series, 2010-01-0739, 2010.

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6. Hulkkonen T, Hillamo H, Sarjovaara T, and Larmi M. Experimental Study of Spray Characteristics between Hydrotreated Vegetable Oil (HVO) and Crude Oil Based EN 590 Diesel Fuel, SAE Paper No. 2011-24-0042, 2011.

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10. Happonen M, Heikkilä J, Aakko-Saksa P, Murtonen T, Lehto K, Rostedt A, Sarjovaara T, Larmi M, Keskinen J, Virtanen A Diesel exhaust emissions and particle hygroscopicity with HVO fuel-oxygenate blend. Fuel, Accepted sept. 2012.

11. Murtonen T, Aakko-Saksa P, Lehto K, Sarjovaara T, Happonen M, Heikkilä J, Larmi M, Keskinen J. Exhaust emission reduction potential with paraffinic renewable diesel by optimizing engine settings or using oxygenate. SAE Technical Paper Series 2012-01-1590, 2012.

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Appendix 1: Paraffinic high cetane number diesel fuels in arctic conditions

Esa Väisänen

Aalto University

Acronyms

CFPP	Cold Filter Plugging Point
CO	Carbon monoxide
CO_2	Carbon dioxide
CP	Cloud point
EGR	Exhaust Gas Recirculation
EVE	Extreme value engine
FAME	Fatty Acid Methyl Ester
F-T	Fischer-Tropsch
HFO	Heavy fuel oil
HVO	Hydrotreated vegetable oil
H_2	Hydrogen
LFO	Light fuel oil
NO_x	Nitrous oxides
MDO	Marine diesel oil
PM	Particulate Matter
SCR	Selective Catalytic Reduction
SO_x	Sulphuric oxides

1 Introduction

With marine and industrial power generation applications it is very important that machinery can be always operated reliably. Present fossil fuels and engine technology have proven to fulfill the reliability requirements, but rising oil prices and more stringent emission regulations make usage of new alternative fuels more attractive. These two are the reasons why alternative fuels are searched and developed also for marine applications. To meet the future emission regulations, one option is to apply exhaust gas after-treatment systems, but these rather expensive investments can be avoided, at least partly with high grade fuels.

A lot of research has been made about first generation biodiesel - fatty acid methyl esters (FAME). Goal has been to find a replacement for fossil diesel and in legislation, term "biodiesel" has been defined as FAME based fuel. But FAME has quite a few problems which limit its use to just a component of diesel fuel. These problems include acid properties, poor cold properties and poor storage stability and increased NO_x-emissions. Also the properties and quality of FAME varies rather much based on raw material.

Since FAME cannot replace fossil diesel in large scale, other alternative has been found. Paraffinic Fischer-Tropsch (F-T) fuels are known to be high quality fuels but their price has been very high compared to traditional diesel fuel. Recently, a method to produce fuel from vegetable oil with very similar properties to F-T fuels, by hydrotreatment have been introduced. These fuels are more commonly known as hydrotreated vegetable oils (HVO) and the best known commercial HVO product is NExBTL by Neste oil Corporation. At the moment there is very little published material on cold properties of these new diesels and information is quite scattered.

There is a need for more information of these new paraffinic, high cetane number and sulfur free diesels, when they are beginning to become common. Use at automotive sector has already started and it may in near future spread wider, maybe to ships. These fuels have many advantages compared to other marine fuels. One of the most important things is that they do not produce SO_x -emissions. Therefore use of exhaust gas after-treatment, like SO_x -scrubbers, is not needed for these emissions in the future, when regulations get stricter. Another important aspect on these new renewable fuels, is their biodegradability properties – especially on vulnerable arctic environments.

2 Paraffinic diesel fuels

Paraffinic hydrocarbons are in many ways very good components of diesel fuel. They are also by themselves very good fuel. Only drawbacks of paraffinic hydrocarbons are lack of lubricity and their tendency to crystallization on lower temperatures. Both these properties can be easily improved by same additives that are used with low sulfur diesel fuels and by altering process parameters.[1]

Paraffinic diesel fuels have been produced for decades in restricted markets. First method of producing paraffinic diesel is through synthesis called Fischer-Tropsch (F-T). With this method, high quality diesel can be produced by gasification from natural gas, biomass or coal. Second method for producing paraffinic diesel is by hydrotreating of vegetable oil. Animal fats can also be used as feedstock in this quite novel method. The paraffinic fuel produced with this method is commonly called HVO. [2]

These two methods produce high quality diesel fuel. Fuels produced by both methods consist primarily of paraffinic hydrocarbons and have very similar chemical structure and physical properties, so it can be presumed that their cold properties are also very similar. [3]

Major advantage of these fuels is that they are similar enough to fossil diesel fuels. Physical properties of these fuels are so near traditional fossil diesel fuel that paraffinic diesel can meet EN590 standard, which is European standard for high grade automotive diesel fuel. Typically the densities of these paraffinic fuels, is the main property causing problems to meet the EN590 standard.[3] In ships, this means that these fuels are comparable to light fuel oil (LFO), and are even superior by some combustion affecting properties. Properties of HVO, Gas to Liquid Fischer-Tropsch fuel, EN590, FAME and CWA 15940 are presented in table 1. CWA 15940 is pre-standard for paraffinic automotive fuels.

Table 1. Typical properties of HVO, European EN 590:2004 diesel fuel, GTL, FAME and CWA 15940:2009. [1,4]

	HVO	EN 590 (summer grade)	GTL	FAME (from rape seed oil)	CWA 15940 Class A
Density at 15 °C (kg/m^3)	775 ... 785	≈ 835	770 ... 785	≈ 885	770...800
Viscosity at 40 °C (mm^2/s)	2.5 ... 3.5	≈ 3.5	3.2 ... 4.5	≈ 4.5	2,0...4,5
Cetane number	≈ 80 ... 99	≈ 53	≈ 73 ... 81	≈ 51	>70
Distillation range (°C)	≈ 180 ... 320	≈ 180 ... 360	≈ 190 ... 330	≈ 350 ... 370	
Cloud point (°C)	−5 ... −25	≈ −5	−0 ... −25	≈ −5	≈-5
Heating value, lower (MJ/kg)	≈ 44.0	≈ 42.7	≈ 43.0	≈ 37.5	
Heating value, lower (MJ/l)	≈ 34.4	≈ 35.7	≈ 34.0	≈ 33.2	
Total aromatics (wt-%)	0	≈ 30	0	0	<1
Polyaromatics (wt-%)[1]	0	≈ 4	0	0	<0,1
Oxygen content (wt-%)	0	0	0	≈ 11	
Sulfur content (mg/kg)	< 10	< 10	< 10	< 10	<5
Lubricity HFRR at 60 °C (µm)	< 460[2]	< 460[2]	< 460[2]	< 460	<460
Storage stability	Good	Good	Good	Very challenging	

[1] European definition including di- and tri+ -aromatics
[2] With lubricity additive

These fuels have many advantages, when compared with fossil diesel fuel. Firstly, they have very high cetane number, which represents ignition capability of the fuel. High cetane number is an advantage at cold starts, but also allows aggressive miller-timing and high EGR rate without major drawbacks on soot emissions. Miller-timing means that intake valve is closed early. This lowers temperature in the cylinder and therefore reduces NO_x -emissions. With aggressive miller-timing and high EGR, the high cetane number is advantageous, because of poor ignition conditions in the cylinder.

NO_x -emissions can be significantly reduced without expensive after-treatment systems, if these techniques are used. According to emission tests, NO_x -emissions and particulate emissions decrease significantly also by just changing the fuel. Reduction of particulate emissions is based mainly on absence of aromatic content, which are precursor for particulate formation. [1, 3]

Engine tests on a medium speed diesel engine have been made in Aalto-university. Engine in question is called extreme value engine (EVE), which is single cylinder research engine with electro hydraulic valves. With different valve timing and HVO, NO_x -emissions were reduced by approximately 50 % without greatly increasing fuel consumption. This reduction is not enough to meet strictest emission regulations, but further optimization may decrease NO_x even further. HVO has also been tested with high speed research engine in Aalto-university. Results were similar, which can be seen in figure 1.

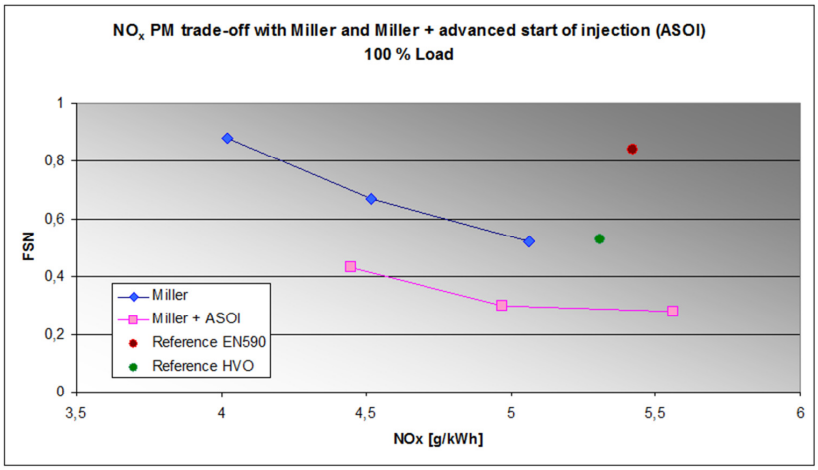

Figure 1. Emissions with HVO on high speed research engine.

Secondly, these synthetic diesels do not contain sulfur. With zero sulfur content, there will be no SO_x -emissions and therefore no after-treatment of those emission components is needed. When regulations considering SO_x -emissions get tighter, switching to paraffinic fuel would be easy, since its similarity to LFO, and investment for after-treatment system would be unnecessary.[1]

2.1 Hydrotreated vegetable oil

Hydrotreated vegetable oil (HVO) is produced from different kinds of vegetable oils such as rape or palm oil. Animal fats can also be used as feedstock. HVO should not be confused with raw vegetable oils, which have wholly different properties and behave more like heavy fuel oil (HFO). Finnish company Neste Oil Oyj is producing HVO with marketing name NExBTL. Process for manufacturing NExBTL is presented here as an example.[3]

Process has pretreatment and two main phases. First, pretreatment, where impurities are separated from vegetable fats and triglycerides are formed. This pretreatment consists of processing with phosphoric acid, sodium hydroxide and water. Process forms sludge, which is then moved to intermediate storage.

After pretreatment, sludge is moved to unit where hydrotreatment is performed. In this unit, fatty acids are converted into n-paraffins, with presence of catalyst. Temperature in this stage is 330-450 °C and pressure

50 bar. After hydrotreatment, isomeration process is performed to gain needed cold properties. In isomeration process, alters the structure of n-paraffin molecules. Isomeration process should not be kept on for too long, because it would result in lower cetane number. Temperature is close to previous step's temperature and pressure is 35-40 bar. Resulting products are diesel fuel and other byproducts. Figure 2 illustrates basic principle of HVO refining process. [3,5]

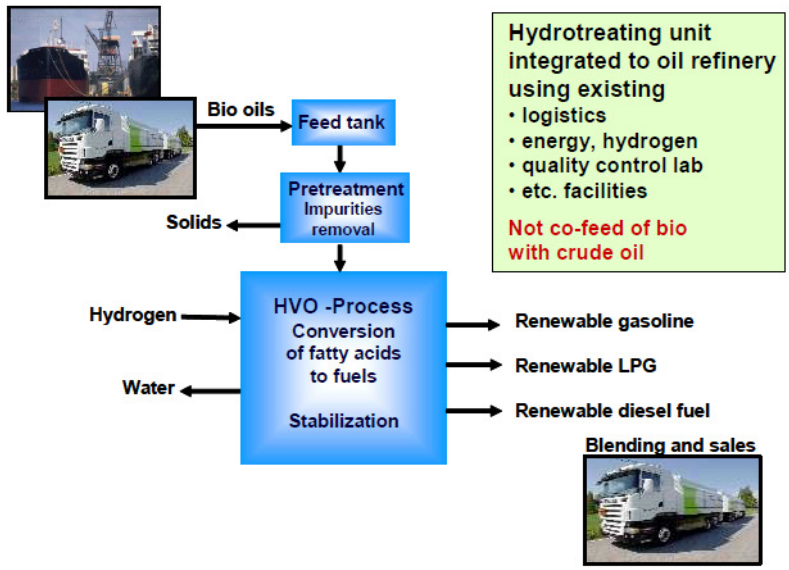

Figure 2. HVO-unit. In addition to the renewable diesel fuel also some biobased hydrocarbon-type gasoline and gases are produced. [3]

2.2 Fischer-Tropsch fuels

Basic principle of Fischer-Tropsch synthesesis is to produce hydrocarbons from carbon monoxide and hydrogen. This method was discovered in 1925 and has been used when crude oil is not available. Reaction needs synthesis gas which can be obtained from many sources, like coal, natural gas or biomass. By changing reaction parameters and catalyst, different products can be produced. These products include gasoline, diesel and kerosene.

Fischer-Tropsch reaction is not particularly efficient and is most suitable when crude oil is not available and coal or other cheap feedstocks are

available. Although reaction is energy consuming, it is possible to reduce produced greenhouse gases by using biomass as a feedstock.

Production process is the same for all feedstocks and consists of gasification, gas cleaning and Fischer-Tropsch reaction. At first phase, synthesis gas is generated from feedstock by gasification. Gasification means that feedstock is partially oxidized. Gas is then cleaned from impurities.

This synthesis gas, which consists of CO and H_2, is then turned into paraffinic hydrocarbons in Fischer-Tropsch synthesis. Catalyst in the reactor is commonly cobalt or iron based, depending on used temperature. With iron based catalyst, higher temperature (350 °C) is used than with cobalt based. With cobalt based catalyst, temperature is about 250 °C. Usable pressure range in the reactor is 10-60 bars. In addition to temperature and pressure, ratio of H_2 to CO in synthesis gas is important parameter of the process. Process works best with the ratio between 0,6 and 2,5. Figure 3 shows principle of F-T fuel production from biomass. [6,7]

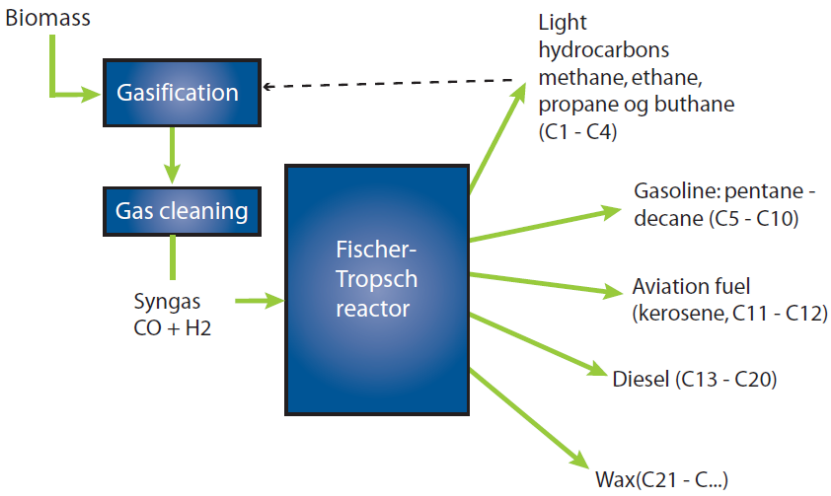

Figure 3. Fischer-Tropsch process [6]

3 Standardized cold properties of diesel fuels in automobile use

Cold properties of diesel fuels can be clearly evaluated with four basic characteristics. These are cloud point, cold filter plugging point, viscosity and pour point. These properties are describing how well fuel can be pumped, filtered and injected into engine. This is quite natural, because problems of cold temperatures are dependent on delivering fuel to the engine. Another challenge is the cold start properties, which can be affected by cetane number on certain level. But still temperature at the end of compression stroke has to be high enough to evaporate and ignite the fuel.

Temperature where fuel seems to become cloudy (crystallization) when examined with bare eye is called cloud point (CP). Fuel becomes cloudy because solid particles emerge in the fluid. Cloud point is sometimes referred as lowest storage temperature, but according to Wärtsilä [6], fuel should always be kept at 10 – 15 °C higher temperature than cloud point. At cloud point, fuel is still usable, but danger of plugged filter exists. When fuel system is properly designed for low temperatures, fuel can still be used when ambient temperature is below cloud point.

Cold filter plugging point (CFPP) is temperature where so much solid particles have emerged that fuel no longer flows through a fuel filter. At this point, fuel is unusable. CFPP is quite useful when cold properties of diesel fuel are considered. [9] Figure 4 is of plugged fuel filter.

Figure 4. Plugged fuel filter

Viscosity describes fluids ability to flow. In other words, if viscosity is low, fluid flows easily. Viscosity of any oil is always strongly dependent on temperature and therefore viscosity is important factor when cold properties of diesel fuels are considered. Viscosity of fuel has to be in right range when it is entering fuel system of engine. Viscosity of fuel has to be taken into account when designing fuel system's components. [9] Figure 5 presents viscosities of traditional marine as a function of temperature. Minimum storage temperature is marked in the figure with thick line. Area where viscosity should be before fuel pumps (16-24 cSt) is also marked in the figure. This viscosity is reached with gas oil at +5 °C and with HFO at +115 °C.

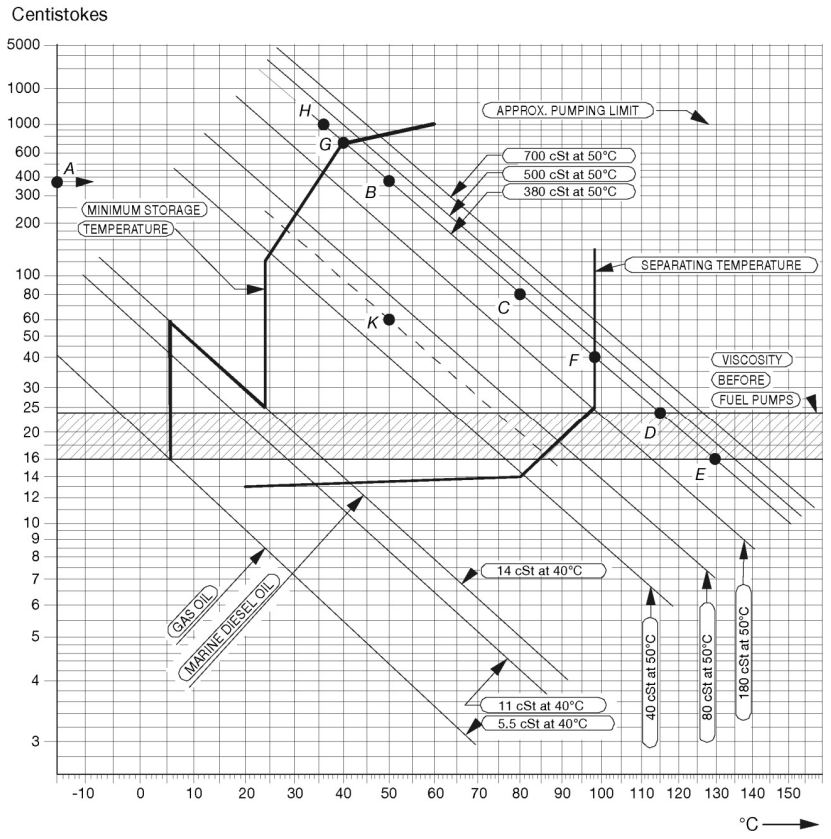

Figure 5. Examples of different fuel viscosities. [10]

Pour point is temperature where fuel no longer flows by its own weight. At this point, fuel is in gel form, containing high amount of agglomerated

crystals.[6] Pour point is not much relevant in automotive use since when fuel reaches pour point, engine has already stopped because CFPP is reached. Table 2 present typical cold property values for diesel fuels.

Table 2. Typical cold property values for diesel fuels.

Typical values	Cloud point	Cold filter plugging point
Diesel, summer quality	-5	-15
Diesel, winter quality	-29	-34
HVO/GTL	-5 ... -40	-5 ... -40

4 Biodegradability, stability and storage

When biofuels are discussed, it is quite obvious that they are made from bio components of some kind. Not so often is noticed if those fuels are biodegradable. Of course it is not main point of biofuels to be biodegradable because fuels are not meant to be discarded to nature. But once in a while, accidents and oil spills occur and then biodegradability becomes important issue.

In this sense, paraffinic diesels are quite simple. They do not contain aromatics or other especially harmful components. This means that they are not really toxic or poisonous.

Biodegradability of paraffinic diesel has not been studied much, but some testing was made as a part of Demonstration of F-T Diesel Fuel in Cold Climates. At these tests, automotive diesel was compared to Fischer-Tropsch diesel. Basically these tests measured CO_2 production from soil samples that were contaminated with fuel. In addition to F-T diesel and fossil diesel also fish based biodiesel was tested. Figure 6 represents cumulative CO_2 production for different soil samples.

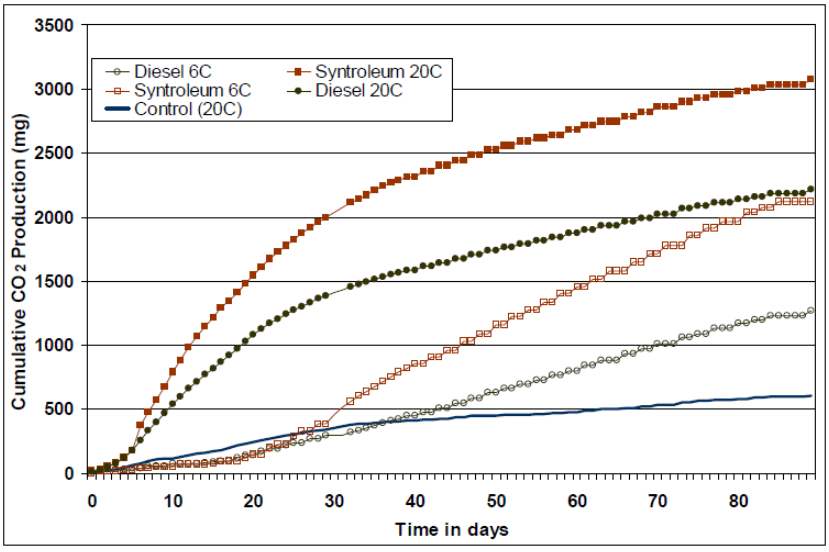

Figure 6. Effect of Temperature on Respiration of Syntroleum F-T v. Diesel, Reported as Cumulative Amount of CO_2 (mg). [2]

The outcome of these tests was that rate of biodegradation of F-T diesel is significantly higher than fossil diesel. This means that F-T diesel is removed from the soil quicker. Another conclusion was that this is result from bacterial action. Temperatures of 6 °C and 20 °C were used in these tests, to find out how temperature affects the process. Significant difference was noticed from start of the experiment, but after short lag phase, rate of CO_2 production was same for both fuels. Later, rate of biodegradation was even higher for 6 °C sample.[2]

FAME based biodiesel is also considered biodegradable. This makes spills of biodiesel easier to cope with and less harmful to environment. Biodiesel degradation in water is shown to be significantly higher than petroleum diesels. These results are applicable also to straight vegetable oils.[6]

One problem which FAME based biodiesel has, is poor storage stability. Because it has oxygen and nitrous components, it is not very stable when stored for a long time. Aging of FAME based biodiesel can increase its corrosiveness and form sediments that may clog filters. Storage conditions such as high temperature, sunlight and oxygen can accelerate ageing. If biodiesel will be stored for longer than 6 to 8 months, oxidation preventive agents should be added. Straight vegetable oil has similar storage properties as FAME based biodiesel. [6]

Neither HVO nor F-T diesel have oxygen or nitrogen, instead they are hydrocarbons which are stable over long time periods. Not much actual results are available about these fuels stability, but at various sources they are considered very stable, like conventional diesel.[3]

5 Paraffinic diesel fuels in cold start and cold use situations in land traffic use

Same characteristics that are measured from traditional diesel fuel, apply also for paraffinic diesels. In general can be said that paraffinic diesel's cold properties are evaluated with similar measures than in case of traditional fossil diesel fuels. In fossil diesel, paraffinic hydrocarbons are limiting factor of low temperature use, because they form wax which cannot flow through filter. When whole fuel consists only of paraffinic hydrocarbons, this problem stays same, but at refining process, temperature where wax starts to appear, can be adjusted.

Paraffinic composition of HVO and F-T diesel affect cold properties of fuel in such way that CFPP and cloud point are nearly identical. This is not necessarily negative, because this makes behavior of fuel quite predictable. With standardized test, the allowed operating temperature can be reliably predicted. [11] Keeping the fuel temperature above cloud point is important to prevent crystallization. With fossil diesel fuels, CFPP can be considerably lower than cloud point. Therefore earlier mentioned 10 – 15 °C higher temperature than cloud point doesn't necessarily apply to paraffinic diesels. To achieve large enough margin to lowest operating point, paraffinic fuel may have to be at even higher temperature than fossil fuel.

Main point of cold properties of these paraffinic fuels is that cloud point is adjustable. Cloud point can be adjusted in HVO between -5 °C and -40 °C.[11] Adjusting is made at refining phase by controlling reaction parameters.

As mentioned before, HVO and F-T diesels have very high cetane number, which makes cold starts easier and reduces emissions formed in them. In "Optibio" project, emission tests in cold start were made. These tests were made on ordinary passenger cars. Results can be seen in figures 7, 8 and 9.[11]

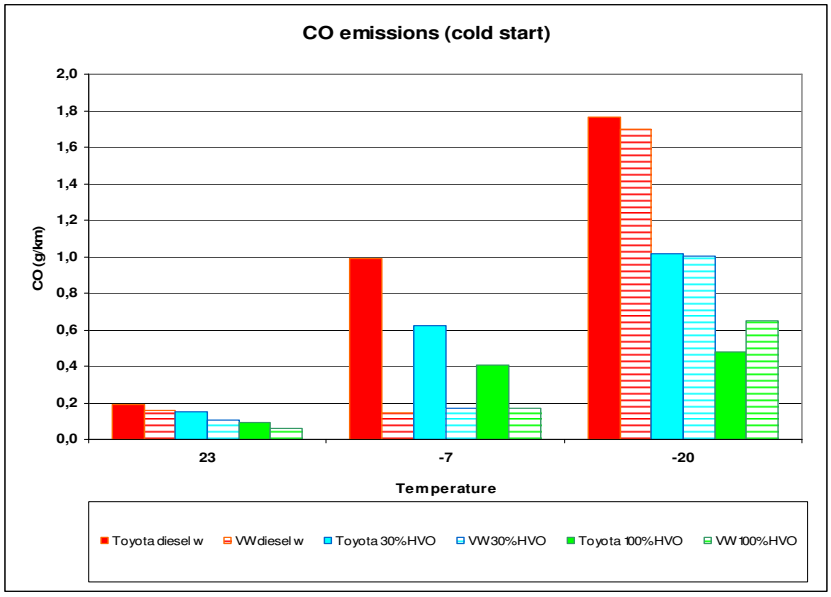

Figure 7. CO emissions at cold start in automotive applications [11]

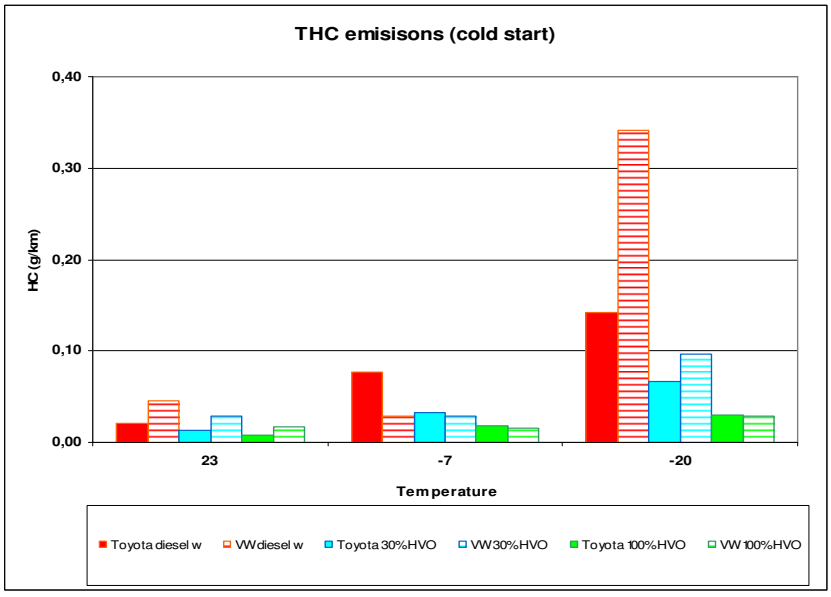

Figure 8. THC emissions at cold start in automotive applications [11]

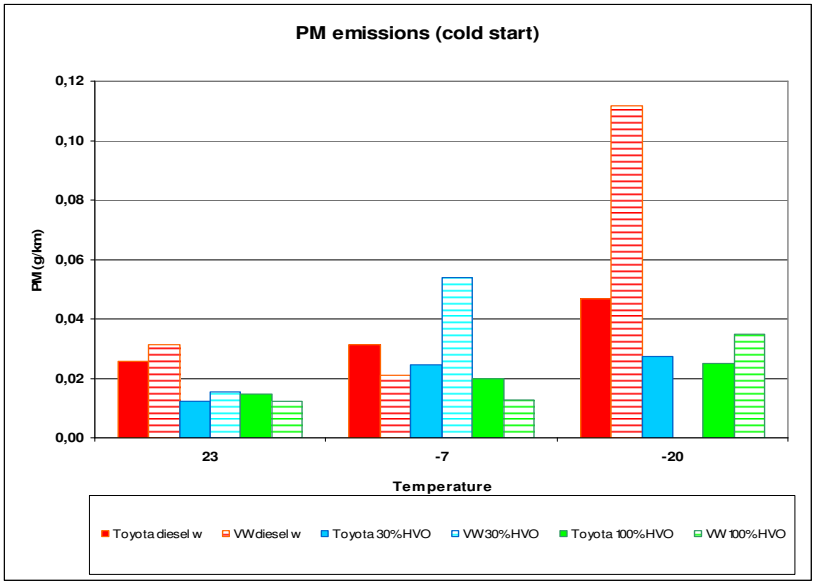

Figure 9. PM emissions at cold start situation in automotive applications [11]

Cold properties of both HVO and F-T diesels have been tested also on the field. Some tests only include low percentage blends, but also tests with neat HVO and F-T diesel have been done.

At Canada, quite wide field tests were made with different kind of bio components. Tests were completed during years 2007 and 2008. During winter, 2% (B2) blend of both FAME and hydrogen derived renewable diesel was used in over 55 trucks. Environment at Alberta, where demonstration took place, is quite harsh. During winter temperature dropped even down to -44 ºC, but fuel caused no problems in everyday situations.[12]

Probably the most extensive tests with HVO were made in project called "Optibio". At this project, neat HVO was used along with 10%, 30% and 50% blends. In addition of tests with local busses, also rig tests were made. This project was first large scale test of high percentage HVO fuel.[11]

Rig tests were made to determine operability of different blends and neat HVO. Rig consisted of fuel pump, filter and tank. Purpose of the test was to measure pressure between pump and the filter. Whole system was first cooled for desired temperature and fuel pump was switched on. After test period of 2000 seconds, lowest pressure between fuel pump and the filter was read. If vacuum achieved 0,7 bars, filter was considered blocked.

Drivability with two passenger cars was also tested in similar conditions. Results for lowest operating temperature for HVO are presented in figure 10. [11]

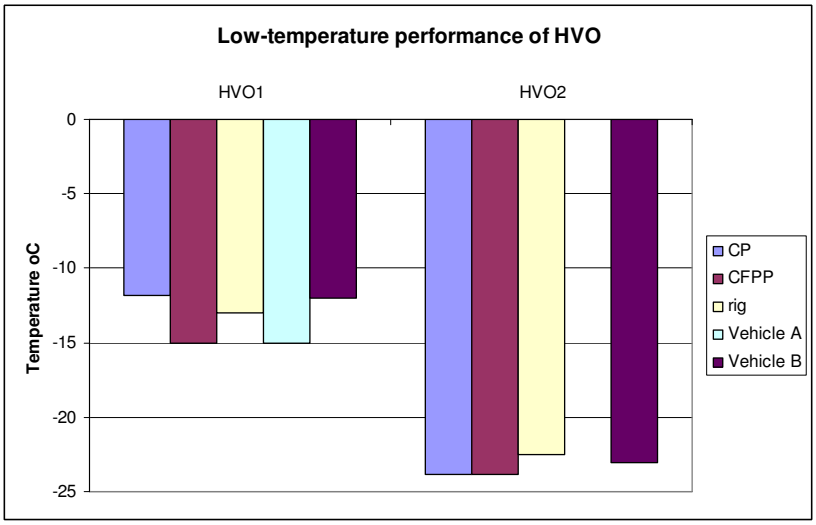

Figure 10. Comparison of CP, CFPP, rig test results and vehicle test results for two HVO grades at Optibio project. CFPPs of HVO1 and HVO2 are -15 ºC and -24 ºC respectively.

All these tests gave quite near results with cloud point and CFPP. Conclusion was that CFPP and cloud point can be used to reliably estimate lowest cold operability. Field tests with local traffic busses were also successful, no problems occurred regardless of exceptional cold winters during the project. [11]

At Fairbanks, Alaska, F-T diesel produced from natural gas was tested in two busses by ICRO (Integrated Concepts and Research Organization) and FTA (Federal Transit Administration). Tests at Fairbanks were carried out during winter 2004-2005. Temperature during winter varied from -40 ºC to 10 ºC. Over all, distance of over 38 000 km was covered.[2]

All of these field tests gave encouraging results. No fuel related problems occurred. This tells at least one thing, that the fuel selection was made well. Selection in this case means selection of cloud point of the fuel and illustrates that no problems occur with right kind of fuel.

6 Marine emission regulations

International maritime organization (IMO) gives regulations to emissions from ships. These regulations contain also other emissions than exhaust gases from engines, for example substances which deplete ozone layer. Here, only short review of engine related emission regulations is presented.

6.1 SO_x

Limits of SO_x -emissions are based on mass percentages of sulfur in fuel. Regulations apply globally, except for emission control areas (ECA), which have even tighter values for emissions. Among few other areas, Baltic Sea is one of control areas. Even though regulation states that fuel has limit for sulfur content, emissions can be decreased to corresponding level by using exhaust gas after treatment, in this case SO_x -scrubbers.

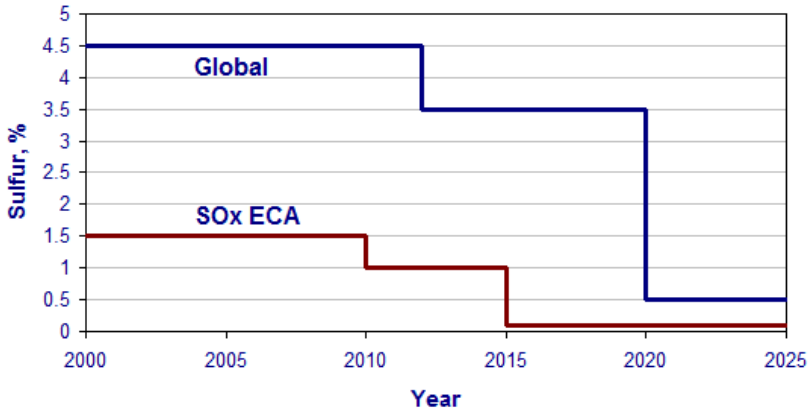

Figure 11. Sulfur content limits for fuel

Figure 11 represents sulfur limits for global and emission control areas. Global limit is now 3,5 % and is going down to 0,5 % at year 2020. In control areas, limit is now 1 % and drops to 0,1 % in year 2015.

Currently, HFO can be used in other than emission control areas. Low sulfur HFO's, which contain 1,0 % sulfur, are available. With these fuels, regulations can be met to year 2015 in control areas and to year 2020 in other areas. After these deadlines, fuel has to be changed to low sulfur MGO or other fuel that has no sulfur, like HVO or straight vegetable oil. Second option is to use SO_x –scrubbers, which remove over 90 % of SO_x -emissions. In this case, use of regular HFO could be continued.[13]

6.2 NO_x

NO_x -emissions are regulated by g/kWh and depend on rated engine speed. Current global regulation is Tier II which is currently met by engine technology. Tier III regulation is however so much stricter, that exhaust after treatment or other additional methods have to be considered. Tier III regulates only control areas and comes into effect in 2016. Figure 12 represents Tier I-III limits for NO_x, according to rated engine speed.

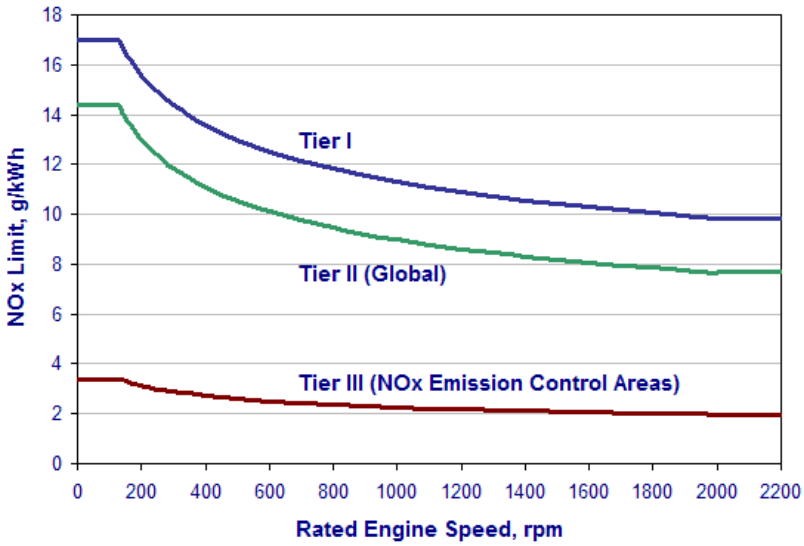

Figure 12. NOx emission limits according to rated engine speed.

NO_x –emissions are originated from air used in combustion. This means that fuel has no straight effect on amount of NO_x –emissions. In some cases fuel can help reduce NO_x –emissions via lowering combustion temperature. This is possible because amount of NO_x –emissions strongly correlate with peak temperature in the cylinder. Peak temperature can be reduced with exhaust gas recirculation (EGR) and miller-timing. Tier II is met currently with these kind of adjustments to engines.

At emission control areas, these kind of measures will not be enough. In this case, selective catalytic reduction (SCR) is needed. SCR is exhaust gas after-treatment system, which reduces NO_x –emissions to Tier III level by catalytic reduction. When SCR is used, engine can be optimized to better fuel economy. Disadvantages of these systems are their size and need of solution which is injected into exhaust.[13]

7 Alternative fuels of near future

7.1 Traditional fossil fuels

In order to continue use of fossil fuels, SO_x - emissions have to be reduced. Easiest option for this is to use low sulfur MDO, which doesn't require any changes to engines and passes the most stringent SO_x -emission regulations. In case of heavy fuels, situation is not so simple. Low sulfur heavy fuels are available, but they also contain so much sulfur that they don't meet regulations which are coming in less than 10 years. This means that with heavy fuels, special SO_x -scrubbers have to be used in the exhaust.

In case on NO_x -emissions, Tier II is already in effect and is met by engine technology. Problem arises in year 2016, when Tier III regulations come into effect. With current fossil fuels, decreasing NO_x -emissions with engine technology would increase fuel consumption significantly. This means that only way to continue use of fossil fuels in control areas is to use exhaust gas after-treatment system, SCR. This kind of system easily reduces NO_x -emissions to Tier III level.

Also blending bio-component to fossil fuel is possible, although it has some problems. This is a mainly a temperature issue, because different fuels need different temperatures to flow properly but too high temperatures can cause polymerization and cavitation in the fuel system. This basically rules out blending straight vegetable oils and HFO. FAME is can be used mainly as a bio-component blended in MDO. Because of lower quality requirements of marine applications, percentage of FAME can be higher than 7%, which is the upper limit in automotive diesel. Blending of bio-component won't solve problems with SO_x and NO_x emissions, but is helpful to fulfill possible CO_2 regulations in the future.

7.2 Liquefied natural gas (LNG)

LNG is natural gas, which has been liquefied by cooling it down to -163 °C. LNG consists mainly of methane, but few other components, such as ethane and propane. In liquid form, LNG is quite safe to transport and does not take so much space than in compressed gaseous form. Flash point of LNG is very high, around 650 °C and area of combustible mixture is very narrow. LNG has to turned into gaseous form before the engine by heating, but

surrounding environment does not cause flow problems as with traditional fuels. These things make LNG very suitable for marine applications.

LNG is good fuel from emissions point of view. It produces significantly less emissions than other fuels, even so much less that it meets Tier III limits without after-treatment systems. This includes both SO_x- and NO_x -emissions. In addition, CO_2 -emissions of LNG are up to 30 % lower than with fossil fuels. This is explained by ratio of carbon to hydrogen, which is significantly lower on LNG than fossil diesel.

Environmental issue with leakage of LNG has two opposite main points. Firstly, in case of leak, LNG will evaporate and will not cause immediate harm to environment. Secondly, methane, which is main component of LNG, is very strong greenhouse gas and will cause harm if released into atmosphere.

Price of LNG is also very low, so it is interesting option as fuel. But because of much room taking storing, usage of LNG will raise ship building costs. Also engine has to be specially made for using gas. Absence of bunkering infrastructure is also preventing LNG usage to become common. Nevertheless, LNG is already in use in LNG hauling tankers.

7.3 Straight vegetable oils

Straight vegetable oils are produced from numerous vegetables and their production in growing. Production is simple, including only extracting of oil from seeds and filtration of impurities. This makes production cheaper and less stressing for environment than much more refined biodiesels or synthetic diesels.

Properties of straight vegetable oils as fuels are resembling HFO. Heating value is little lower than with HFO, but ignition properties are better. Although straight vegetable oils need similar preheating and fuel system than HFO, changing from HFO to vegetable oil needs adjustments to fuel system. Use of straight vegetable oil is already approved by some engine manufacturers and they provide compatible fuel systems for vegetable oils.

Emissions of straight vegetable oils are partly lower than with fossil fuels. Straight vegetable oils don't contain sulfur, so they won't produce SO_x -emissions. Therefore there is no need for SO_x scrubbers. Also fossil CO_2 -emissions are lower, but NO_x –emissions will slightly increase when

straight vegetable oil is used. This means that at emission control areas SCR systems have to be used from year 2016.

7.4 Summary

HVO is one alternative fuel of near future, but other alternatives are also available. These other alternatives have their own advantages and disadvantages, and there may be many good options for different situations, for example, liquefied natural gas (LNG) is very interesting option as a fuel for tankers shipping LNG. It is likely that in the future there are many types of fuels in use, according to environmental regulations and availability of fuels. Table 3 compares different fuel types.

Table 3. Fuel properties, advantages (+) and disadvantages (-).

Fuel	Price	Cold storing	Particle emissions	NOx emissions	CO2 emissions	SOx emissions	Requires new technology	Environmental impact in case of oil spill	Availability in near future
HFO	+	-	-	-	-	-	+	-	+
Low sulfur HFO	+	-	-	-	-	+	+	-	+
Low sulfur MDO	-	+	-	-	-	+	+	-	+
Biodiesel (FAME)	-	-	+	-	+	+	+	+	-
Straight vegetable oils	-	-	+	-	+	+	+	+	-
Synthetic diesel, F-T and HVO	-	+	+	+	+	+	+	+	-
Natural gas, LNG	+	+	+	+	+	+	-	+	+

Alternative fuels are researched mainly because of SO_x and NO_x regulations, which are getting quite strict in less than 10 years and technical solutions to engines won't be enough to meet the requirements. CO_2 -emissions are not yet clearly regulated, but all alternative fuels will reduce CO_2 -emissions, if they are produced efficiently.

As can be seen on table 2, HVO and F-T fuels are superior fuels in technical sense. They reduce all emissions significantly. They do not need new technology or systems and therefore changing fuel is easy. Only LNG is better fuel in sense of emissions, but need of new infrastructure is big disadvantage.

8 New alternatives of power production

8.1 New renewable fuels

One alternative fuel for diesel engines is dimethyl ether (DME), which can be produced from methanol, natural gas, coal or biomass. Also DME is suitable as diesel fuel because it has high cetane number. DME also produces less emissions than traditional diesel, burns clean and is good fuel for diesel engines in many senses.

DME is gaseous in normal conditions and it has to be pressurized to make it liquid, therefore storing is more difficult than with traditional diesel. Heating value of DME is also considerably lower than with diesel fuel, which makes it inefficient as a fuel. Use of DME is on experimental stage on trucks. There are similar ethers which could be used as a fuel, but DME seems to be the most promising one.

Although group of alcohols is wide, most common alcohols used as a fuel are methanol and ethanol. Other alcohols, such as butanol, are currently under development as fuels. Methanol and ethanol are suitable for internal combustion engines, but because of their very low cetane number, they are more suitable to gasoline than diesel engines. This means that if diesel fuel would be simply replaced with alcohol, engine would have to be considerably different. Especially fuel system and cold start systems would have to be completely different. Fuel systems capacity also has to be higher, because alcohols have considerably lower heating value than diesel.

Option to blend alcohols with diesel fuels is also difficult approach. Blend of alcohol and diesel tends to separate and pick-up water. To solve this problem, additives have to be used. To make alcohols work on diesel engines, large amount of ignition improvers are also needed. Alternative also exists to use dual-fuel system, where alcohol has completely own fuel system and diesel is used to ignite mixture in the cylinder. With dual-fuel systems, alcohols could be used as a main fuel without drawbacks of blending or simple alcohol use, but these kind of systems are not ready to commercial use.

8.2 Fuel cells

Fuel cell is power production method which is still on experimental level. Main operating principle of fuel cell is to produce electricity through oxidation reaction of hydrogen. Fuel cells are divided to main types according to used electrolyte. PEM-type cells use pure hydrogen and are suitable for smaller energy needs. SOFC- and MCFC-cells are more suitable for bigger energy needs and they can use big variety of fuels if special reforming unit is used.

Fuels used in fuel cells can vary widely. Diesel fuel, alcohol, LNG and hydrogen are all possible fuels. If hydrogen is used, fuel cell does not need complex reformation unit, but storing of hydrogen is taking much space, because hydrogen has very low energy density. As fuel, hydrogen would be optimum for fuel cells, but with current technology, hydrogen is not an option for bigger ships, because of the storage issue.

Other fuels, such as diesel, are much easier to storage, but reformation unit has to be installed. Preparation and reformation of MDO for fuel cell use is difficult because its chemical structure is not uniform and it contains sulfur. LNG is in this sense much easier to use with fuel cells, but same storing problems have to be dealt with as in engine use. If these hydrocarbon based fuels are used, reforming process also produces CO_2-emissions.

Fuel cells are often considered as a possible replacement of engines in the future. However, fuel cells have some big disadvantages which make them still insufficient as main power source of ships. First disadvantage is low power of current units, which is in range of below 1 MW. Second important disadvantage is poor ability to respond to load changes. Also, the power density of fuel cells is very low, meaning that need for space would be huge, many times that of an engine. Adding to this space need would be large electric motors needed for propulsion, as fuel cells produce only electricity and heat.

Apart from poor functional properties, fuel cells are expensive, partly because they need precious metals as catalysts. These metals include gold and platinum, which are the most expensive metal on earth. At current fuel cells, catalyst is not even everlasting, but has to be changed after certain time.

In near future, use will be limited to part of ships auxiliary power production. When more powerful units come to market, one possible use could be auxiliary power when ship is in harbor. Fuel cells advantages are that they are quiet and do not produce SO_x or NO_x -emissions nor particles.[13]

9 Summary

Although paraffinic diesel fuels have been produced for a long time (F-T fuels), their usage has been limited because of high price. In the near future usage of these fuels will increase. Although their excellent properties as fuels, it hasn't been the reason for their increasing production. Main reason is tightening greenhouse gas emission legislation which gives these fuels an advantage, when produced from bio feedstock. Future NO_x, soot and SO_x emission regulations may be met with present fossil fuels to some extent – especially with after-treatment systems, but when fossil CO_2 -emissions become regulated, alternative fuels have to be used at least as blends.

Few options are in sight to replace present fossil diesel fuels and diesel engine technology. Although for example gas engines are already usable, they have their own disadvantages, mainly related to storing of the gas. Perfect solution would be alternative fuel, which can be used in present and future engines with minor modifications and this fuel would help to meet the emission regulations. For this purpose, paraffinic diesel fuels are excellent.

Paraffinic diesel fuels can be produced with Fischer-Tropsch synthesis, or by hydrotreating vegetable oil. These both methods produce basically same very high quality diesel fuel. Advantages of these paraffinic fuels are numerous, and can be said that they are best diesel fuels available.

When usage in ships is considered, it is simple to compare paraffinic diesels to light fuel oil. By many properties, paraffinic diesels are even much better than light fuel oils. They do not contain impurities such as sulfur or aromatic hydrocarbons, which makes them good option as a future low emission fuel. Only drawback of these fuels is their high price, but as oil price goes up, they also become relatively cheaper. Also the production capacity of HVO and F-T fuels is strongly increasing, which should make them more competitive economically.

Cold properties of HVO and F-T fuels are excellent, when compared to HFO. They don't need heating before the engine, as long as temperature is kept above cloud point. Cloud point is adjustable at refining phase by changing process parameters. In this way, cloud point can be set as low as -40 °C.

Cold properties of these fuels can be evaluated in same manner as in light fuel oils and automotive diesels. This is done with few characteristics, most important ones being cloud point and CFPP. It is important to notice, that paraffinic diesel fuel's cloud point and CFPP are almost identical, unlike with fossil diesel fuel. This means that operability at low temperatures is quite easily evaluated simply by cloud point. Although, for the same reason, the storage temperature marginal to cloud point, might have to be higher than with LFO

Field tests have been made at various locations and with both blended and neat fuel. All these tests gave encouraging results, as no fuel related problems occurred. This proves that evaluation of operability can be reliably made with just cloud point, which was in tests selected carefully.

As light fuel oil, also the paraffinic fuels are less hazardous than HFO, when spilled to nature. This is because HFO forms viscose masses, which are hard to remove, and may be heavier than water. Lighter fuels also tend to evaporate and degrade much faster, which is the case especially with HVO and F-T diesels. In fact paraffinic fuels degrade even faster than light fuel oils.

As a conclusion paraffinic diesel fuels have very similar cold properties with LFO, but as advantage:

- exhaust gas raw emissions are typically lower
- they are always sulfur free
- they are more biodegradable than traditional fossil fuels
- fossil CO_2 emissions are lower than with fossil fuel, depending on feedstock

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Appendix 1.1: ISO 8217:2010 Standard for marine fuels

MARINE DISTILLATE FUELS

Parameter	Unit	Limit	DMX	DMA	DMZ	DMB
Viscosity at 40°C	mm^2/s	Max	5.500	6.000	6.000	11.00
Viscosity at 40°C	mm^2/s	Min	1.400	2.000	3.000	2.000
Micro Carbon Residue at 10% Residue	% m/m	Max	0.30	0.30	0.30	-
Density at 15°C	kg/m^3	Max	-	890.0	890.0	900.0
Micro Carbon Residue	% m/m	Max	-	-	-	0.30
Sulphur [a]	% m/m	Max	1.00	1.50	1.50	2.00
Water	% V/V	Max	-	-	-	0.30 [b]
Total sediment by hot filtration	% m/m	Max	-	-	-	0.10 [b]
Ash	% m/m	Max	0.010	0.010	0.010	0.010
Flash point	0°C	Min	43.0	60.0	60.0	60.0
Pour point, Summer	0°C	Max	-	0	0	6
Pour point, Winter	°C	Max	-	-6	-6	0
Cloud point	°C	Max	-16	-	-	-
Calculated Cetane Index		Min	45	40	40	35
Acid Number	mgKOH/g	Max	0.5	0.5	0.5	0.5
Oxidation stability	g/m^3	Max	25	25	25	25 [c]
Lubricity, corrected wear scar diameter (wsd 1.4 at 60°C [d]	um	Max	520	520	520	520 [c]
Hydrogen sulphide [e]	mg/kg	Max	2.00	2.00	2.00	2.00
Appearance			Clear & Bright [f]			[b, c]

a	A sulphur limit of 1.00% m/m applies in the Emission Control Areas designated by the International Maritime Organization. As there may be local variations, the purchaser shall define the maximum sulphur content according to the relevant statutory requirements, notwithstanding the limits given in this table.
b	If the sample is not clear and bright, total sediment by hot filtration and water test shall be required.
c	Oxidation stability and lubricity tests are not applicable if the sample is not clear and bright.
d	Applicable if sulphur is less than 0.050% m/m.
e	Effective only from 1 July 2012.
f	If the sample is dyed and not transparent, water test shall be required. The water content shall not exceed 200 mg/kg (0.02% m/m).

MARINE RESIDUAL FUELS

Parameter	Unit	Limit	RMA [a]	RMB	RMD	RME	RMG				RMK		
			10	30	80	180	180	380	500	700	380	500	700
Viscosity at 50°C	mm^2/s	Max	10.00	30.00	80.00	180.0	180.0	380.0	500.0	700.0	380.0	500.0	700.0
Density at 15°C	kg/m^3	Max	920.0	960.0	975.0	991.0	991.0				1010.0		
Micro Carbon Residue	% m/m	Max	2.50	10.00	14.00	15.00	18.00				20.00		
Aluminium + Silicon	mg/kg	Max	25	40		50	60						
Sodium	mg/kg	Max	50	100		50	100						
Ash	% m/m	Max	0.040	0.070			0.100				0.150		
Vanadium	mg/kg	Max	50	150			350				450		
CCAI	-	Max	850	860			870						
Water	% V/V	Max	0.30	0.50									
Pour point (upper) [b], Summer	°C	Max	6				30						
Pour point (upper) [b], Winter	°C	Max	0				30						
Flash point	°C	Min	60.0										
Sulphur [c]	% m/m	Max	Statutory requirements										
Total Sediment, aged	% m/m	Max	0.10										
Acid Number [e]	mgKOH/g	Max	2.5										
Used lubricating oils (ULO): Calcium and Zinc; or Calcium and Phosphorus	mg/kg	-	The fuel shall be free from ULO, and shall be considered to contain ULO when either one of the following conditions is met: Calcium > 30 and zinc >15; or Calcium > 30 and phosphorus > 15.										
Hydrogen sulphide [d]	mg/kg	Max	2.00										

a	This residual marine fuel grade is formerly DMC distillate under ISO 8217:2005.
b	Purchasers shall ensure that this pour point is suitable for the equipment on board, especially in cold climates.
c	The purchaser shall define the maximum sulphur content according to the relevant statutory requirements.
d	Effective only from 1 July 2012.
e	Strong acids are not acceptable, even at levels not detectable by the standard test methods for SAN. As acid numbers below the values stated in the table do not guarantee that the fuels are free from problems associated with the presence of acidic compounds, it is the responsibility of the supplier and the purchaser to agree upon an acceptable acid number.

Appendix 1.2: CWA 15940:2009 Automotive fuels – Paraffinic diesel from synthesis or hydrotreatment – Requirements and test methods

Table 1 - Generally applicable requirements and test methods

Property	Unit	Limits Class A		Limits Class B		Test method [a] (See 2. Normative references)
		minimum	maximum	minimum	maximum	
Cetane number [b]		70,0 [c]	–	51,0	66,0	EN ISO 5165 EN 15195
Density at 15 °C	kg/m^3	770,0	800,0	770,0	800,0	EN ISO 3675 EN ISO 12185
Total aromatics content [c]	% (*m/m*)	–	1,0	–	1,0	EN 12916 UOP 495 SS 155116
Polycyclic aromatic hydrocarbons content [c,d]	% (*m/m*)	–	0,1	–	0,1	EN 12916 UOP 495 SS 155116
Total olefin content [c]	% (*m/m*)	–	0,1	–	0,1	ASTM D1159 ASTM D2710 [e]
Sulfur content	mg/kg	–	5,0	–	5,0	EN ISO 20846 EN ISO 20884
Flash point	°C	> 55	–	> 55	–	EN ISO 2719
Carbon residue [f] (on 10 % distillation residue)	% (*m/m*)	–	0,30	–	0,30	EN ISO 10370
Ash content	% (*m/m*)	–	0,01	–	0,01	EN ISO 6245
Water content [g]	mg/kg	–	200	–	200	EN ISO 12937
Total contamination	mg/kg	–	24	–	24	EN 12662
Copper strip corrosion (3 h at 50 °C)	rating	class 1		class 1		EN ISO 2160
Oxidation stability	g/m^3	-	25		25	EN ISO 12205
Lubricity, corrected wear scar diameter (wsd 1,4) at 60 °C [h]	µm	–	460		460	EN ISO 12156-1
Viscosity at 40 °C	mm^2/s	2,00	4,50	2,00	4,50	EN ISO 3104
Distillation 95 % (*V/V*) [i] recovered at	°C		360		360	EN ISO 3405

[a] See also 5.6.1

[b] See also 5.4.2 and 5.6.3

[c] See also 5.6.2

[d] For the purposes of this Workshop Agreement, polycyclic aromatic hydrocarbons are defined as the total aromatic hydrocarbon content less the mono-aromatic hydrocarbon content, both as determined by EN 12916. Esters, being used at low levels as a lubricating agent, may have an interference effect.

[e] To determine the total olefin content Annex A.2 of ASTM D1159 shall be used for both test methods

[f] See also 5.4.3

[g] In general, paraffinic diesel fuel is clear and bright at visual inspection at the point of sale.

[h] In the future, based on actual marketing monitoring and on request of the purchaser, lowering to 400 µm is possible. The paraffinic diesel fuel producer is advised, with regards to the actual test method's precision, to aim his production at that level.

[i] For the calculation of the cetane index the 10 %, 50 % and 90 % (*V/V*) recovery points are also needed.

Appendix 2 - Diesel oxygenates – literature and selection

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Contents

1. Introduction

Oxygenates are considered as diesel fuel components due to their capability to reduce exhaust emissions. Oxygenates based on renewable feedstocks would also help with climate change and energy security challenges. The optimum diesel oxygenate would be compatible with unmodified compression-ignition engines and infrastructure.

The compression-ignition diesel engine is the leading power source for the heavy-duty engines due to its high efficiency. In Europe, diesel engines are increasingly popular in the light-duty cars, as well. However, drawbacks of diesel engines are high emissions of particulate matter and nitrogen oxides. Oxygenates may offer one solution to reduce these emissions, especially as concerns diesel particles.

Many studies have covered a comprehensive set of oxygenates, e.g. Pecci et al. (1991) some 80 oxygenates, Delfort et al. (2002) 18 oxygenates, Natarajan et al. (2001) 71 oxygenates. In addition, numerous studies have focused on specific oxygenate groups. The best-known diesel oxygenates at the moment are fatty acid methyl esters, FAME.

In this study, focus is given to fuel properties of oxygenates and their impact on the exhaust emissions, whereas production aspects are not discussed. The objective is to cover oxygenates, which are compatible with conventional diesel engines, and which can effectively reduce particulate matter emissions. In the final discussion of this review, one oxygenate is selected for the experimental part of project.

2. Particulate matter emissions with oxygenates

2.1 General theory

For diesel engine, NO_x and particulate matter emissions are bottlenecks. Several emission control technologies can be used to tackle these emissions, for instance EGR and SCR to reduce NO_x emissions and diesel particulate filters to reduce particulate matter emissions. In addition, fuel composition can be modified to reduce exhaust emissions.

In the automotive engines, the dominating process for NO_x formation is oxidation of nitrogen in air at high temperatures (Zeldovich mechanism)[1]. In older engines, increase in fuel viscosity advance *injection timing* leading to higher combustion temperature and NO_x emissions. However, differences in flame temperatures of components may overrule the differences in viscosities, for instance aromatic hydrocarbons have higher flame temperatures than paraffins and alcohols. The *heat of evaporation* of the fuel affect the NO_x emissions, as well. For instance, *evaporation of alcohols cools air-fuel mixture*.

Particle formation occurs in the rich zones in the fuel jet via pyrolysis of the fuel. Particle nuclei consisting of carbon grows both through coagulation and absorption of hydrocarbons. Water and sulphates adhere onto the surface of the particles. The composition of particulate matter varies depending on the engine technology, test conditions, and the contents of sulphur and aromatics in the fuel. In general, non-aromatic fuels with simple chemical structure and short carbon-carbon chain, e.g. methane, burn cleanly. The major part of diesel exhaust particles originates from the fuel. However, the lubricating oil is also an important factor with today's engine technology and high quality fuels.

[1] Typical nitrogen content of diesel fuel does not significantly contribute in the NO_x emission from current diesel engines. For example, 30 mg/kg nitrogen content in fuel theoretically leads to NO_x emission below 0.02 g/kWh, approximately. (Editorial).

Reduction in particulate matter emission is achievable by modifying hydrocarbons of fuel, and also by introducing oxygenates as diesel components. Fuel aromatics content, distillation characteristics, cetane number and oxygen content are important parameters as regards exhaust emissions. In addition, fuel viscosity and density may affect injection timing, fuel spray and evaporation, and consequently, exhaust emissions. Especially in older engines with fully mechanical injection systems, changes in fuel density affected NO_x and PM emissions. In new engines, injection systems are electronically controlled, and fuel properties do not influence the start of injection. A combination of modified diesel fuel and oxygenate together with emission control technologies may result in a good emission performance. (Boot *et al.* 2009, Yeh *et al.* 2001).

Generally, *oxygenates reduce particulate matter* emission. Gonzales (2001) observed that total particulate matter emission reduced on average 26% for fuels containing 7 wt-% oxygen. Karas (1994) reported that for glycol ethers, *1 wt-% oxygen content of fuel resulted in 15% reduction in particulate matter emission*. Hess (2000) refers to studies, in which *1% oxygen content resulted in 3-5%, 4-10% or even 67% reduction* in particulate matter emissions by using glycol ethers. Boot *et al.* (2009) reported that *soot-free combustion is achievable at 30-40 wt-% oxygen content of fuel.*

Particulate matter emissions reduce when fuel contains oxygen, but this is not a linear phenomenon.

- Functional group may overrule the effect of oxygen content.
- Engine, load and emission control characteristics play a role.

Favourable oxygenate chemistry:
- Short carbon chains.
- Linear carbon chains.
- Symmetrical position of oxygen in ethers.
- However, cetane number, density, viscosity, distillation etc. are important, as well.

A number of mechanisms have been presented to explain the effect of exygenates on particulate matter emission. A general theory is that oxygenated fuels bring oxygen in the mixing-controlled flame, which reduces soot formation. (Delfort et al. 2002). Oxygenates change also properties of fuel, e.g. viscosity, which affects injection timing and spray characteristics. Declining cetane number increases ignition delay, and consequently, the increased amount of fuel burns in premixed mode. (Boot et al. 2007). In mixing-controlled combustion, soot is formed when fuel burns close to stoichiometry.

Bertoli et al. (1997) reported that soot emission reduced substantially with glycol ethers with an increased flame temperature. This also led to moderate increase in NO_x emission. Increase in aldehyde and carbonyl emission could be expected with oxygen containing fuel, but an opposite result was seen in this study. This could be explained with over-lean mixture zone and high cetane number combined with high combustion temperature.

Janssen *et al.* (2009) studied theory of soot formation and oxidation by using decanol as fuel. Soot emissions reduced up to 90% depending on load point. The mechanism for this was thought to be as follows a) Thermal mechanism based on *locally reduced temperatures* due to higher evaporation heat of 1-deconol in the reaction zone where soot appears. b) OH-radicals, *oxidation molecules*, are available earlier in *rich and high temperature zones*. Soot oxidation starts already in the phases of soot formation.

Ren (2007) observed that smoke emission decreased 3.7% for 1 wt-% of oxygen in the fuel containing diglyme. Ignition delay and temperature increased by addition of diglyme. Hess (2000) reported that diglyme shortens duration of combustion, with a shift towards diffusion phase combustion. Huang *et al.* (2003) observed that the smoke emission decreased with dimethyl carbonate (DMC), but NO_x emission was not influenced. Premixed combustion was prolonged, whereas the diffusive combustion was shortened with DMC. In addition, the maximum of the cylinder pressure, the rate of pressure rise and the rate of heat release increased, especially at medium and high loads.

Serdari (2000) assumes that lower Bosch smoke number than 0.5 can be achieved with higher fuel oxygen to carbon ratio than 0.2. This was studied also by Hashimoto *et al.* (1991) by using dimethylacetal as oxygenate.

Natarjan (2001) referred to a study, in which particulate matter emission followed hydrogen to carbon ratio curve with hydrocarbons fuels, but not with oxygenated fuels (Figure 2.1). Carbon atoms tied with oxygen might not participate in the particulate matter formation. Gonzales (2001) reported that dry particulate matter emission seemed to correlate with effective hydrogen to carbon ratio of oxygenate, which takes into account how strongly oxygen is bonded to carbon. This did not necessarily apply to total particulate matter emission[2].

[2] Total particulate matter emission consists of many substances, for example, soot, hydrocarbons and sulphates. So called “dry” fraction of particulate matter emission

Yeh *et al.* (2001) reported that lower boiling oxygenates were more effective than higher boiling oxygenates in the reduction of particulate matter emissions.

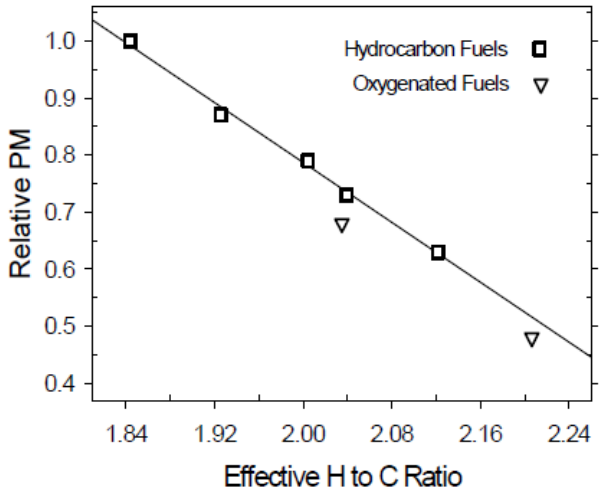


Figure 0.1. Relationship between hydrogen to carbon ratio of fuel and particulate matter emission (Natarajan 2001).

2.2 Impact of oxygenate structure

Delfort et al. (2002) concluded in a study with light-duty direct-injection car that the *effect of oxygenate on the particulate matter emission depends primarily on the functional group. Within each functional group, oxygen content is a key parameter* as regards particulate matter emission (Figure 2.2). The best performances were observed with fuels having the highest oxygen contents, but some low-oxygen fuels reduced particulate matter emission almost as much as the high-oxygen fuels.

is obtained by removing soluble and/or volatile fractions from total particulate matter. (Editorial).

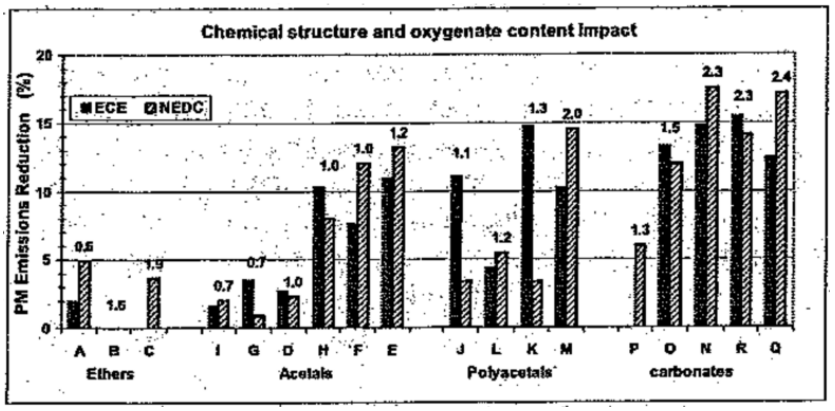


Figure 0.2. The effect of oxygen is important within each chemical group of oxygenates (Delfort et al. 2002).

Karas (1994) reported that all oxygen containing compounds do not reduce particulate matter emissions effectively. E.g. 1-phenyl ethanol, 1-cyclohexyl ethanol, and methyl soyate were ineffective when compared to *diethers or glycols*. Boot *et al.* (2007) also observed that two fuels showed similar particulate matter emission even though the other fuel had twice the oxygen content of the other fuel.

Xu et al. (2006) studied combustion behaviour with FILE technique at constant-volume chamber for oxygenate with C-O-C bonds (TPGME) and for an ester with O-C=O bond (DBM). For TPGME soot appears later during premixed period even if fuel autoignites earlier, but for DBM less soot is observed during mixing controlled period due to longer lift-off length and more oxygen entraint from ambient air. Overall, *TPGME was efficient at premixed combustion, whereas DBM at mixing controlled combustion*. In addition to oxygen in fuel, the role of *oxygen entrained from ambient was significant*. Oxygenated fuels resulted in less soot through combustion period without significant differences in combustion phasing or heat release.

Frijters et al. (2006) studied combustion of glycol ethers (TGM, TPGME), dibutyl maleate, ethanol and RME with heavy-duty engine. Cetane numbers between fuels were smoothen by using cetane improver for ethanol and RME. The results showed that *particulate matter reduction increases faster at low oxygen contents, and levels off for higher oxygen contents*. At low oxygen levels, significant differences in capability to reduce particulate matter emissions were observed between different oxygenates. When

blended with Fischer-Tropsch paraffinic fuel, oxygenates resulted in especially low particulate matter emissions.

An example of the effect of the structure of oxygenated fuels on particulate formation in diesel engines is shown in Figure 2.3. Particulate matter emissions were significantly reduced and the oxygenate structure was determining factor in addition to the oxygen content in the fuel (Bowman 2006).

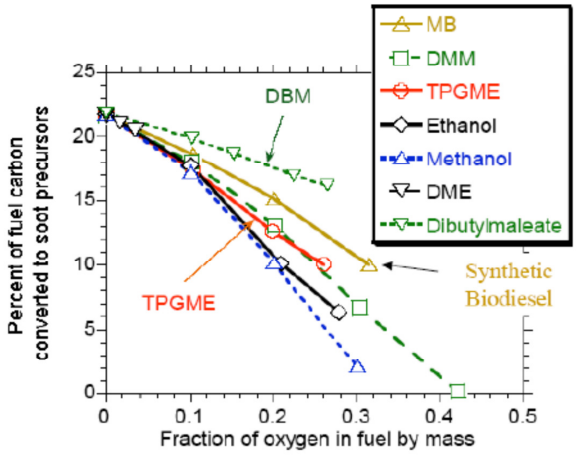


Figure 0.3. Relationship of sooting tendency and oxygen content of fuel obtained with different oxygenates (Bowman *et al.* 2006, Westbrook and Pitz 2002).

Studies claiming that C-O bonds are the most effective in soot reduction

Some studies report low soot emissions for glycol ethers, in which each oxygen atom is connected to two carbon atoms (C-O-C). McCormic (2002) presents a theory that anti-sooting effects of fuel depends on distribution of oxygen atoms in molecule. *Molecules with C-O bonds remove one C atom per O atom, whereas esters remove one C atom per two O atoms as CO_2.* Mueller *et al.* (2003) concluded that 30% of oxygen in ester is unavailable for eliminating soot precursors, and thus glycol ether (TPGME) is more effective in soot reduction than dibutyl maleate ester.

Yeh et al. (2001) studied the effect of functional group of oxygenates by using ethers, esters, alcohols and carbonates at 2 wt-% oxygen level. Ethers and alcohols were more effective than carbonates and esters in reducing particulate matter emissions, and *C9-C12 alcohols* were the most effective

oxygenates. It was thought that *oxygen in carbonates and esters are not likely to break free*. In addition, in ethers and alcohols a higher fractions of carbon atoms have a C-O bond than in carbonates and esters. No significant difference was seen in particulate matter emission when using *branched or linear* high-molecular weight esters.

Studies claiming that esters (O-C=O) are most effective in soot reduction

Boot *et al.* (2009) reported that esters are the most efficient soot reducing oxygenates. Also Frijters et al. (2006) reported that maleate (DBM) is more effective than glycol ether (TPGME) in reduction of particulate matter emission.

Delfort et al. (2002) reported that *oxygen in carbonates was more effective than oxygen in acetals or ethers*. Comparison of ethoxyethyl carbonates to diethyl carbonate showed that reduction of particulate matter emission originated primarily of the carbonate group of oxygenate, not from the ether group. Comparison was conducted also with tetrahydrofurfyryl derivatives.

Gonzales (2001) assumed that strong oxygen-carbon bond prevents carbon to involve efficiently into soot formation.

One study claims that soot reduction efficiency is highest when 1) oxygen is in the middle of ethers and carbonyls, and for other oxygenates when carbon chain is short 2) no branches exit in the carbon-chain 3) reaction pathways should produce ethylene[3] and methyl radical instead of larger alkenes. (McEnally and Pfefferle 2011).

2.3 Engine parameters

The effect of oxygenates on emissions may depend on engine parameters and adjustments. Boot *et al.* (2009) concluded that the importance of cetane number and role of oxygenate increases at high EGR ratios. Lower particulate matter emission with lower cetane number oxygenates was observed. Delfort *et al.* (2002) found no direct relation between oxygenate cetane number and particulate matter emission. Some oxygenates with low cetane numbers showed high particulate matter reductions, and some high-cetane oxygenates showed low particulate matter reductions. Particulate

[3] Ethylene is known as soot precursor. (Editorial).

matter emissions were studied with direct-injection passenger car with 18 oxygenates as 5 vol-% concentration in diesel fuel.

Boot *et al.* (2007) observed that the ability of oxygenates to reduce particulate matter emissions depends on *load*, which might be related to changes in air-to-fuel ratio and combustion temperature. *At high loads, benefit of oxygen may diminish*. An opposite phenomenon was reported by Giavazzi *et al.* (1991). Cetane number seemed to be the determining fuel factor at lower loads, whereas *oxygen content seemed be significant at higher loads*. Nabi and Hustad (2010) reported also that smoke reduction with oxygenates was higher at higher loads.

3. Oxygenate options

3.1 General properties of oxygenates

A number of different oxygenates have been considered as components for diesel fuel, or to be used as such in a compression ignition engines. These oxygenates include various alcohols, ethers, esters and carbonates. Table 1 shows chemical structure of oxygenate groups and some examples of individual oxygenates.

Table 3.1. The general structure of oxygenates.

R-OH	*Alcohols*
R-O-R	*Ethers*
R-O-R-O-R	*Glycol ethers*
R-O-C-O-R	*Acetals*
R-C(=O)-O-R	*Esters*
R-O-C(=O)-O-R	*Carbonates*

R, hydrocarbon chain; C, carbon; O, oxygen

There are a number of fuel properties, both physical and chemical, which are important for the proper operation of a diesel engine. Regulations and standards control diesel fuel quality. In Europe, Fuel Quality Directive 2009/30/EC and standard EN 590 set the basic requirements for the diesel fuel properties. In addition, the auto- and engine manufactures have published their recommendations for fuel quality requirements (the World Wide Fuel Charter, WWFC). Diesel fuel requirements should met even when oxygenates are used as blending components at reasonable blending ratios.

The fuel properties of oxygenates depend on, e.g., length and type of alkyl chains. Oxygenates with higher molecular weight often have higher density, higher boiling point, higher viscosity, better lubricity, lower volatility, and lower flammability than respective oxygenates with lower molecular weight. Therefore, oxygenates with higher molecular weight are preferred as diesel fuel components.

3.1.1 Ignition quality

The diesel process is based on auto-ignition of the fuel. Thus ignition properties of oxygenates are of primary importance. Ignition quality of fuel is described by cetane number. High cetane number leads to e.g. shortened ignition delay, increase in duration of combustion and lower peak pressure. In general, poor ignition quality leads to improper combustion and increased exhaust emissions. The European Directive 2009/30/EC requires a minimum cetane number of 51 for European diesel fuel. Ignition improver additives may increase cetane number to some extent.

As concerns hydrocarbons, normal alkanes, called straight-chain paraffinis, have the highest cetane numbers, whereas aromatics have the lowest cetane numbers. Ignition quality improves as the chain length increases (Figure 3.1). This applies also to oxygenates with same functional groups and similar branching of alkyl chain.

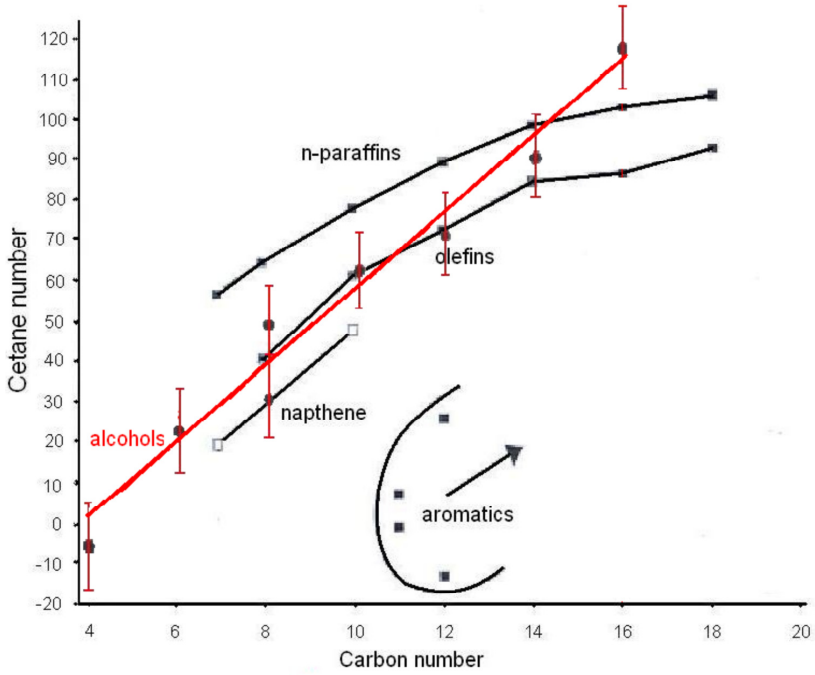


Figure 0.4. The effect of molecular size on cetane number. (data by Shell Lexikon, Stournas *et al.* 1993).

Pecci *et al.* (1991) reported that blending cetane number increases with increasing alkyl chain up to *di-n-hexyl ether*. Branching of the alkyl chain depresses cetane number of oxygenates. The highest cetane number was observed for molecules with three ether groups in structure (e.g. glycols). Position of oxygen atoms show complex behaviour, but molecules with oxygen atom at central or omega positions tend to show the highest blending cetane numbers. Cetane numbers of esters are quite modest, but they increase with the length of the carboxylic acid alkyl chain.

3.1.2 Flash point, distillation

Flash point is the limit temperature for the formation of an ignitable air-fuel vapor mixture. Storage and handling regulations for fuels are based on the flash point. In Europe, flash point of diesel fuel must be higher than 55 °C. Fuel with lower flash point is handled as gasoline.

Distillation range of diesel fuel is around 180-340 °C. New components should fall into this range to ensure proper combustion in diesel engine. Traditional analysis methods are not always suitable for oxygenates. Distillation methods for oxygenates are discussed by Smith *et al.* (2008).

3.1.3 Miscibility, water tolerance, stability, engine wear and corrosion, peroxide formation

Hydrocarbons, especially alkanes, are non-polar compounds, whereas oxygenates are polar in nature. This may result in various compatibility problems. The most polar oxygenates, e.g. methanol and ethanol, are not miscible with diesel fuel without additives. Less polar oxygenates, for instance n-pentyl ether, are miscible with diesel fuel. Miscibility depends on the chemical structure, oxygen content and on the physical properties of substances (“like dissolves like”). Miscibility of oxygenates also depends on the hydrocarbon constituents of diesel fuel. Aromatics, for example, are more polar than paraffins. Therefore increasing aromatics content of diesel fuel may improve the solubility of oxygenates. (McCormic 2001).

Hydrocarbons are addressed with poor water-solubility. Oxygenates are typically much more polar compounds than hydrocarbons, and consequently, water-affinity of oxygenates is higher than that of diesel fuel. In addition, oxygenates tend to be hygroscopic, absorbing water from ambient air. In diesel engine, water may cause problems. For instance,

phase separation risk is considerable for many oxygenates, and this is promoted at low ambient temperatures. Corrosion of materials may occur with oxygenates.

Proper lubricity of fuel is also an important requirement. Lubricity can be improved with additives, however, not in the presence of very aggressive compounds, such as acids.

3.1.4 Density, heating value, viscosity, aromatics, sulphur, cold properties

Diesel fuel injection system is based on volumetric principle. Therefore lower density of fuel typically leads to reduced maximum power output and higher volumetric fuel consumption. This may be compensated by higher energy content of fuel. Energy content of oxygenates is typically lower than that for hydrocarbon fuels due to oxygen content.

Low viscosity of fuel may cause fuel leakages, whereas high viscosity of fuel may over-load the injection system.

Aromatics and sulphur content are important parameters as regards exhaust emissions. Typically, oxygenates do not contain aromatics or sulphur.

Pecci *et al.* (1991) reported that cold properties of oxygenates improve with increased branching, and worsen with increasing number of oxygen atoms. However, this behaviour is non-linear. Monoethers with C$\geq$10, for example *di-n-pentyl ether*, offer a compromise between cetane number and cold properties.

3.6 Alcohols

3.6.1 Methanol and ethanol

Low-molecular weight alcohols, methanol and ethanol, are not suitable blending components in diesel fuel for conventional diesel engines (Aakko and Nylund 2004, BIOSCOPES). Adding ethanol into diesel worsen major part of the fuel properties. Additives are needed firstly to keep diesel/ethanol as a blend, and secondly

CH_3OH	Methanol
C_2H_5OH	Ethanol
C_4H_9OH	Butanol

to bring critical fuel properties like cetane number and lubricity even to minimum acceptance level. However, the major problem of diesel/ethanol blends are related to flash point and flammability limits with safety concerns for fuel handling, storage and use. Methanol is even more unsuitable diesel component than ethanol. Some studies have covered mixtures of ethanol, diesel fuel and/or biodiesel, also in combination with new combustion processes (Sebastian and Nagarajan 2010, Hu *et al.* 2006, Shudo *et al.* 2005, Huang *et al.* 2004, Mohammadi *et al.* 2004, 2005).

Neat ethanol with ignition improver additive can be used in modified diesel engines. For example, ethanol buses manufactured by Scania are used in Sweden. (Scania's online information).

3.6.2 Butanol

Boiling points of butanol isomers, 82-118 °C, are low when compared to distillation range of diesel fuel. Wadumesthrige *et al.* (2010) reported that when 10 vol-% butanol is blended with diesel fuel, both cetane number and lubricity fall below requirements. A blend containing 10 vol-% FAME and 10 vol-% butanol in diesel fuel meets the ASTM requirements for cetane number, viscosity and lubricity, but flash point (44 °C) is still below the limit.

Valentino *et al.* (2012) studied blends with 20% and 40% n-butanol in diesel fuel in high-speed, common rail, direct-injection diesel engine equipped with EGR. The injection pressure, intake oxygen content and injection timing was adjusted to premixed combustion. NO_x and smoke emissions were lower for blends than for diesel fuel. For blends, cetane numbers were lower, volatility higher and resistance to auto ignition higher than for diesel fuel.

Zöldy *et al.* (2010) tested butanol as diesel extender. Butanol as 5 vol-% blend without cetane improver was otherwise a good option for diesel engine, but flash point of blend was unacceptable.

3.6.3 Heavier alcohols

A commercially available Swedish fuel called Agrodiesel 15 contains 15% of renewables consisting of 5% rapeseed methyl ester and 10% *heavy alcohols*. The blend is a stable solution, which meets diesel standards (Petterson 2005, Golubkov 2005). Heavy-duty engine tests have shown e.g. lower

particulate matter and PAH emissions with Agrodiesel 15 than with Swedish Environmental Class 1 diesel fuel. A long-term test of 500 hours showed no excessive wear and no engine failures during the test. A field test of one year with buses performed well. Oil analyses and engine inspections revealed no problems. Drivers felt that odour of Agrodiesel 15 was stronger than that of hydrocarbon diesel. Some comments stated that the buses run with slightly less power with Agrodiesel 15 than with diesel fuel. (Petterson 2005).

Yeh *et al.* (2001) found that isodecanol was the most efficient oxygenate in reducing particulate matter emission. This study included various esters, carbonates, alcohols and ethers at 2 wt-% oxygen level. A substantial amount of isodecanol is needed to achieve 2 wt-% oxygen content in fuel. One fuel was blended with respective amount of a paraffinic component (Isopar™) for comparison. Paraffinic component reduced particulate matter emission to some extent, but not as effectively as isodecanol.

Janssen *et al.* (2009) reported that 1-decanol seem to be beneficial for advanced combustion systems. Soot emissions reduced up to 90% depending on load point.

Karas (1994) reported that not all oxygen containing compounds reduce effectively PM emissions. E.g. heavy alcohols, 1-phenyl ethanol and 1-cyclohexyl ethanol were ineffective when compared to diethers or glycols.

3.7 Ethers, acetals and ketones

3.7.1 Low-molecular weight ethers

Dimethyl ether (DME) is a low-molecular weight ether, gaseous fuel at normal temperature. DME needs to be slightly pressurised before usage in modified diesel engine with redesigned of fuel pumps and fuel injectors. (Chapman *et al.* 2003).

Diethyl ether (DEE) has also been studied as diesel fuel extender, e.g by Subramanian *et al.* (2009), Cheng *et al.* (2002) and Bailey *et al.* (1997). Several studies considered dimethoxymethane (DMM) as diesel fuel extender (Arteconi et al. 2011). Boiling points of these ethers are very low, 35 °C for DEE and 42 °C for DMM.

CH_3-O-CH_3	C_2H_5-O-C_2H_5	CH_3-O-CH_2-O-CH_3	$(C_2H_5$-O$)_2$-C_2H_4
Dimethyl ether (DME)	Diethyl ether (DEE)	Dimethoxymethane (DMM)	1,1-Diethoxyethane

A thesis by Nord (2005) includes a study by using acetal (1,1-dietoxyethane) as fuel in diesel engine. This acetal can be made from ethanol. However, acetal is a light compound with a boiling point of only 103 °C and flash point of -20 °C.

3.7.2 Di-n-butyl ether and ethoxy ethanol

Beeckmann *et al.* (2010) studied *di-n-butyl ether* (DBE) as diesel fuel component. Boiling point of DBE, 141 °C, is close to distillation range of diesel fuel, but flash point is low (25 °C). (Arteconi *et al.* 2011). Delfort *et al.* (2002) studied DBE and other oxygenates with direct-injection car. 5 vol-% of DBE resulted in a 5% reduction in particulate matter emission.

C_4H_9-O-C_4H_9
Di-n-butyl ether (DBE)

C_2H_5-O-C_2H_4OH
2-Ethoxy ethanol

Subramanian et al. (2009) studied *2-ethoxy ethanol* as diesel fuel extender in 2.5, 5 and 7.5 wt-% blends. This oxygenate was effective in terms of exhaust emissions. Boiling point of 2-ethoxy ethanol is 135 °C.

3.7.3 Di-n-pentyl ether, DNPE

Pecci *et al.* (1991) concluded that symmetrical and asymmetrical mono-ethers seem to give the best compromise between cetane characteristics and the behaviour at low temperature. Murphy (1999, 2002), found *di-n-pentyl ether (DNPE)* as a potential oxygenate for blending into diesel fuel.

C_5H_{11}-O- C_5H_{11}
Di-n-pentyl ether, DNPE

Cetane number of *di-n-pentyl ether* (DNPE) is high (103-153) and other properties are diesel-like. DNPE is fully soluble in diesel fuel. Solubility of DNPE in water is low. DNPE is 15 times more biodegradable than another

fuel ether, MTBE. Marchionna (2001) reported that DNPE could be produced from methane via propylene oxide. This would allow production of DNPE from waste-based biomethane. DNPE can be also produced by a selective process from n-butane. (Marchionna *et al.* 2000) and by hydration of 1-pentanol, which results in over 90% yield (Tejero *et al.* 2006).

Giavazzi (1991) reported that DNPE is favorable fuel component as regards engine performance. With 17% DNPE blends, particulate matter emissions reduced in the tests with passenger car. Martin *et al.* (1997) concluded that DNPE behaves with the same trend as high cetane paraffinic hydrocarbons.

Marchionna *et al.* (2000) reported of emission tests by using 10% and 20% DNPE blends with light-duty car and heavy-duty engines. In the car tests, DNPE reduced particulate matter emissions by nearly 10%. CO, HC and air toxic emissions reduced, as well. Emission benefits were observed also under cold conditions. For the heavy-duty engine, particulate matter, CO and HC emissions reduced by 15-20%, and NO_x emission by 2-2.5% with 20% DNPE blend (Figure 3.2).

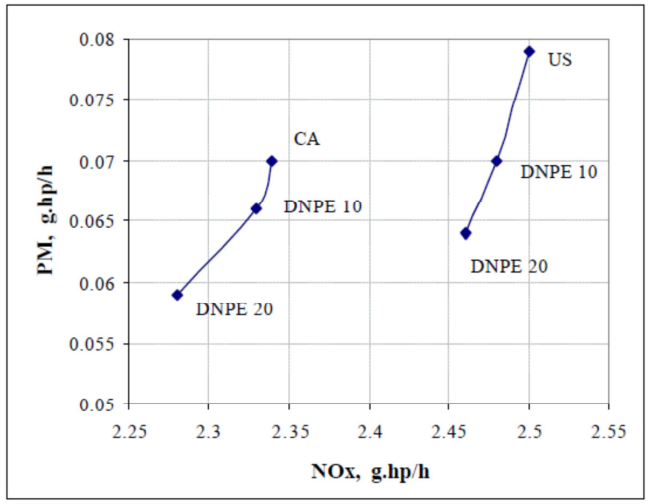
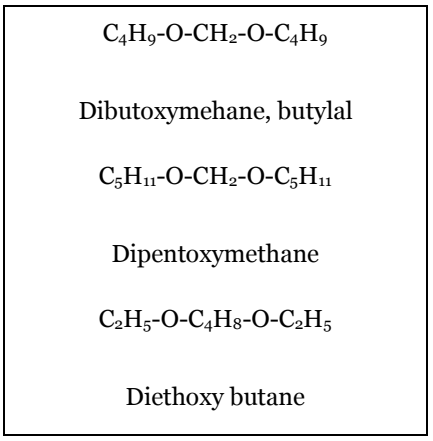


Figure 0.5. Trade-off between PM and NO_x emissions by using DNPE as diesel fuel component for the heavy-duty engine. (Marchionna 2000).

3.7.4 Dibutoxy methane (butylal) and some other acetals



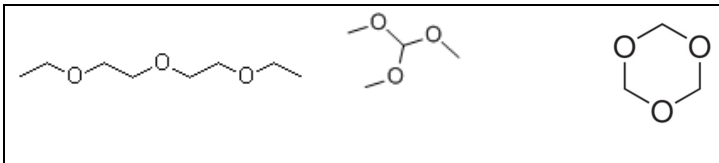
According to Ryu *et al.* (2000) poly-ethers or ethers with high molecular weight are better diesel fuel components than mono-ethers. Murphy (1999, 2002) found that *dibutoxymethane* (butylal, $C_9H_{20}O_2$) is soluble with diesel fuel, and it could be a potential oxygenate for blending into diesel. Boiling point of butylal is 180 °C and flash point is 62 °C.

Bertola *et al.* (2000) reported of different diesel-butylal mixtures. Lubricity of butylal is poor, and thus lubricity additive was used. In the engine tests, *butylal reduced exhaust opacity and did not increase NO_x emission*. Premix combustion rate and the combustion noise were lower with butylal than with diesel fuel, which was thought to be due to high cetane number of butylal (>74). Butylal was concluded to be a promising diesel oxygenate.

Giavazzi (1991) reported that *di-n-pentoxy methane* (DNPM) is favourable fuel component as regards engine performance. Boiling point of DNPM is 218 °C, and cetane number is high (97). Other properties of DNPM are diesel-like. In the tests with passenger car, particulate matter emissions reduced with fuel containing 25% DNPM when compared to diesel fuel.

Diethoxy butane is mentioned as an interesting diesel oxygenate, which has high cetane number (97). However, flash point of this oxygenate is rather low (45 °C). *Diethoxy butane* could be produced from ethanol (dehydration -> diethyl ether -> oxidative coupling) or by using fossil butadiene. (McCormick *et al.* 2002).

Delfort et al. (2002) studied ten acetals and polyacetals with direct-injection car. The most significant particulate matter reductions, from 8 to 15 %, were achieved with blends containing 5 vol-% of di-ethoxy-1,1-pentane, di-ethoxy-1,1-butane, di-ethoxy-1,1-propane or di(ethoxy-2-ethyl)polyoxomethylene. These fuels contained 1-2 wt-% oxygen.



2-Ethoxy ethyl ether Trimehoxymethane Trioxane

McCormick *et al.* (2002) reported that *2-ethoxy ethyl ether* (diethyl carbitol) has interesting fuel properties, but he also mentioned that this oxygenate exhibits unacceptable toxicological properties. However, Murphy (1999) found *2-ethoxy ethyl ether* as potential fuel oxygenate.

Yeh *et al.* (2001) included trioxane, a cyclic ether, and trimethoxy methane, in the engine testing program, in which isodecanol was found as the most effective oxygenate in the reduction of particulate matter emission.

Snamprogetti's "oxy-diesel" is processed via oligomerisation of DMM. These *poly-oxy-methylenes* are similar to diesel, without volatility or flash point problems. They are more biodegradable than MTBE and production costs are low. (Hart Diesel Fuel News 2001).

MAN Truck & Bus and Emissionskonzepte Motoren has analysed synthetic fuels of the type *oxymethylene ether (OME)* as diesel fuel additives, which are relatively easy to synthesize from methanol. (Lumpp *et al.* 2011).

3.7.5 Glycerol derivatives

Glycerol is formed as a side-product in FAME production. One interesting option would be using glycerol derivatives as fuels. Glycerol can be a feedstock in etherification to produce *Glycerol-tert-butyl ethers*, GTBE (Di Serio *et al.* 2010, Figure 3.3). Boot *et al.* (2007) have studied GTBE.

Karas *et al.* (1994) reported of heavy-duty tests with *di-tert-butyl glycerol* together with other oxygenates. Spooner-Wyman *et al.* (2003) concluded that *di-butoxy glycerol* is a promising diesel extender. With this oxygenate, PM emissions decreased, but NO_x emissions increased.

García *et al.* (2008) synthesised an *acetal from glycerine*: 2,2-dimethyl-1,3-dioxalan-4yl)methyl acetate, and a triacetin. However, fuel properties or engine tests were not reported.

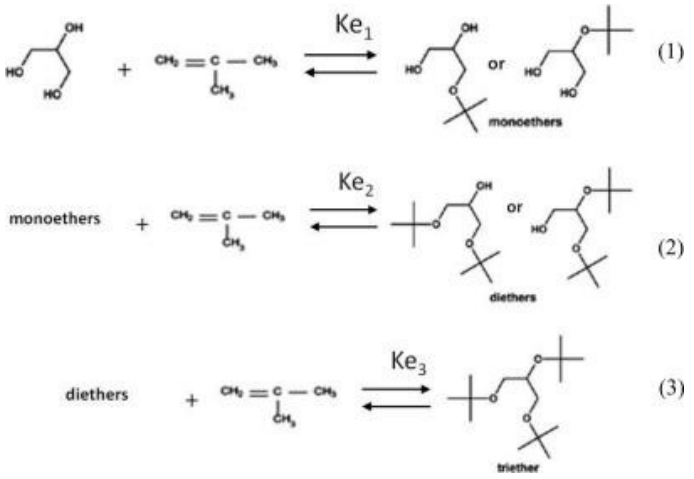


Figure 0.6. Glycerol etherification to Glycerol-tert-butyl ethers, GTBE (Di Serio *et al.* 2010).

3.7.6 Cyclohexanone

Boot *et al.* (2009) studied combustion behaviour of *tripropylene glycol monoethyl ether* (TPGME), *dibutyl maleate,* and *cyclohexanone.* Behavior of cyclohexanone was exceptionally good. Cyclic oxygenates could be made from lignocellulosic biomass.

3.8 Glycol ethers

Glycol ethers can be divided into so called E-series and P-series glycol ethers depending on the synthesis route (Figure 3.4). E-series glycol ethers consist mainly of methyl, ethyl and butyl glycol ethers produced from ethylene oxide. P-series propylene glycol ethers (PGEs) are based on reactions of propylene oxide with alcohols. (Glycol ethers online 2011).

E-series glycol ethers are basically water-soluble, whereas solubility in diesel fuel is poor (Karas 1994). Therefore main attention is given to P-series glycol ethers when diesel fuel extender candidates are studied. Liotta *et al.* (1993) excluded *ethylene* and *propylene glycols* due to poor solubility in diesel fuel.

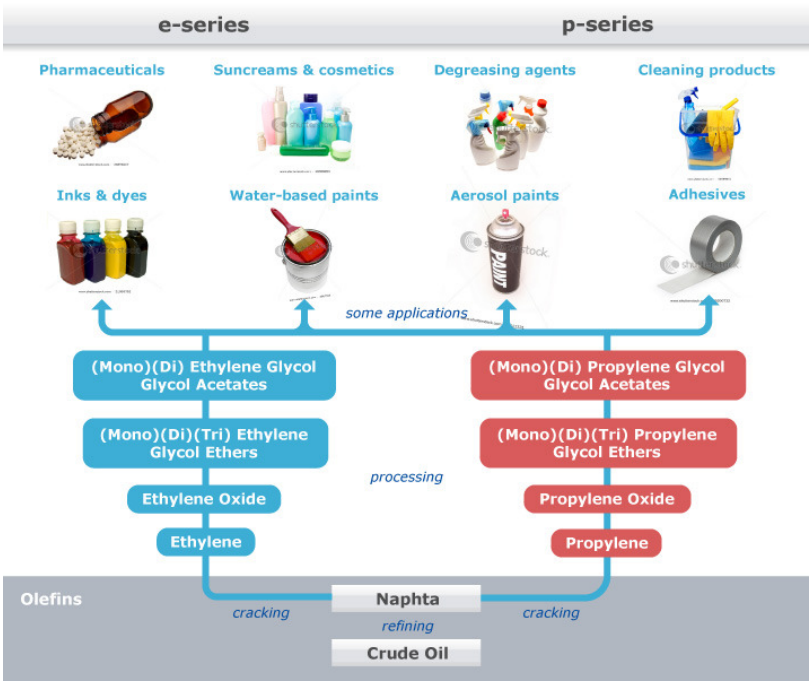


Figure 0.7. E- and P-series glycol ethers (Glycol ethers online 2011).

3.8.1 Monoglyme, diglyme, triglyme, tetraglyme

Many *glycol ethers,* for instance monoglyme and diglyme, have been considered as blending components for diesel fuel. *Monoglyme* (*ethylene glycol dimethylether*) and *diglyme* (*diethylene glycol dimethyl ether*) were earlier known as cetane improvers. These compounds have high oxygen content, high auto-ignition tendency and high cetane numbers. *Glycol ethers* can be manufactured from syngas

C-O-CC-O-C
Monoglyme

C-O-CC-O-CC-O-C
Diglyme

C-O-CC-O-CC-O-CC-O-C
Triglyme

C-O-CC-O-CC-O-CC-O-CC-O-C
Tetraglyme

through dimethyl ether (DME) synthesis (Hess *et al.* 2000).

Natarajan *et al.* (2001) excluded some *glymes* from the list of potential oxygenates due to problems in solubility, water tolerance or corrosion. Karas *et al.* (1994) mentioned that *diglyme* is addressed with health problems, and production is expensive. Arteconi *et al.* (2011) also reports of substantial health and environmental risks related to diglyme.

Natarajan (2001) referred to a study of 90's reporting that 1 wt-% oxygen obtained with glymes result in 6-7% reduction in particulate matter emission. *Diglyme* increased NO_x emission by 2%. Ren *et al.* (2007) and Loganathan *et al.* (2007) observed beneficial effect of *diglyme* on engine performance, smoke emission and NO_x emissions. Zhu *et al.* (2003) reported that in the tests with a light-duty diesel truck, *diglyme* (14.4 vol-%) reduced PM, THC and CO emissions. Particulate matter emission was reduced by 20-40%. Blending diglyme in diesel fuel did not increase NO_x emissions and toxic compounds in exhaust, such as benzene, butadiene, formaldehyde and PAHs.

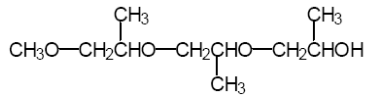
Hess *et al.* (2000) studied the CETANER™ with Cummins ISB 5.9 litre turbocharged DI diesel engine. At 15% concentration, mixture of 20/80 *monoglyme* and *diglyme*, reduced PM emission by 42% and NO_x emission by 8.8%. At above 15% CETANER™ addition, the engine was unable to reach peak power output. Cetane number of CETANER™ is greater than 100.

Kozak *et al.* (2007) studied exhaust emissions with Euro 4 passenger car by using 5 vol-% blends of six glycol ethers: *glyme, diglyme, triglyme, tetraethylene glycol dimethyl ether, diethylene glycol dibutyl ether and dipropylene glycol dimethyl ether*. Glycols reduced effectively PM, CO and HC emissions, but NO_x emission increased approximately by 2-8%. Oxygenates represented close to 2 wt-% oxygen contents in fuel. Particulate matter emissions were generally dependent on oxygen content of fuel. CO and HC emissions seemed to depend on other fuel properties in addition to oxygen content, e.g. distillation range may be significant. *Diglyme was the best oxygenate tested offering 13% reduction in PM emission, with 2.5% increase in NO_x emission*. Kozak *et al.* (2007) reported that reduction in particulate matter emission was 6-7% for glycol ethers when oxygen content of fuel was 1 wt-% (European test cycle).

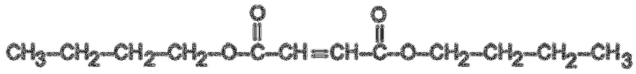
Natarajan *et al.* (2001) referred to literature, in which *tetraglyme* decreased NO_x emission by 2.5%. With *triglyme* and *tetraglyme,* particulate matter emission reduced by 5-6.5%.

Nabi and Hustad (2010) studied *diethylene diglyme* and jatropha biodiesel at oxygen level of 2.26 wt-% in diesel fuel. Tests were conducted with Scania Euro II engine. Maximum smoke reduction with *diglyme* was 38%, but higher reduction of 50% was obtained with *jathropha biodiesel*. Particulate matter emission was reduced close to 30% with both oxygenated fuels. Number of accumulation mode particles were reduced with both oxygenates when compared to diesel fuel. CO and HC emission reduced with these oxygenates, but NO_x emission increased slightly or remained unchange.

3.8.2 Tripropylene glycol monoethyl ether (TPGME) compared to dibutyl maleate (DBM) and alcohols



Tripropylene glycol monomethyl ether



Dibutyl maleate

One of the most extensive general study of oxygenates was carried out by *Natarajan et al.* (2001). In this study, 71 oxygenates were reviewed, of which 8 oxygenates were selected for engine tests. The first criteria was to achieve 7 wt-% oxygen content in blend by using no more than 20 vol-% of oxygenate. This criteria excludes oxygenates with oxygen content below 35 wt-%. The following eight oxygenates were selected for engine tests (Gonzáles *et al.* 2001):

- Tri-propylene glycol mono-methyl ether
- Methoxy-2-propanol
- Di-propylene glycol mono-methyl ether
- 2-Ethoxy ethyl acetate
- 2-Ethoxy ethyl ether
- Di-ethyl adipate

- Tributyrin
- Di-butyl maleate

From these candidates, *tripropylene glycol monomethyl ether* (TPGME) and dibutyl maleate (DBM) were deemed to be the most promising ones (Gonzáles *et al.* 2001). Later on, these oxygenates were studied in several projects.

TPGME is miscible in aromatic diesel fuel, but addition of water may lead to phase separation (Murphy 2002). *TPGME* is not fully miscible with paraffinic Fischer-Tropsch diesel at 30 vol-% concentration. Portions of TPGME molecule are very electronegative, which results in difficulty in mixing in non-polar diesel fuel. *Dibutyl maleate* (DBM) is soluble in diesel fuel, whereas *diethyl maleat*e forms two layers with ultra-low sulphur diesel fuel in 10 vol-% concentration.

Natarajan *et al.* (2001) referred to capability of *diethyl maleate* and *dibutyl maleate* to reduce in-cylinder soot by 12%, and NO_x by 5-8.5% (single-cylinder engine). In direct-injection light-duty engine, opposite results were obtained.

Maleates and carbonates were found to be more effective than glycols in reduction of particulate matter emission in a study with a passenger car (Kozak et al. 2009). This study included seven glycols, two maleates and two carbonates at 5 vol-% concetrations in diesel fuel. These oxygenates reduced particulate matter emission, whereas NO_x emission increased in many cases. The best PM/NO_x trade-off results were achieved with *carbonates* and *maleates*. *Diethyl maleate*, *dimethyl carbonate* and *diethyl carbonate* were selected as the most promising oxygenates. Also Kozak *et al.* (2008a) reported of favourable PM/NO_x trade-off for maleates in the tests with passenger car.

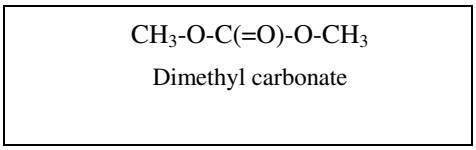
Stoner and Litzinger (1999) reported that *maleates* appear to be more effective than *glycol ethers* in soot reduction. The maleates reduced NO_x emission as well, which was thought to be due to delayed start of combustion. No effect of boiling point of oxygenates were observed.

Mueller *et al.* (2003) reported that *glycol ether (TPGME) was more effective in soot reduction than maleate (DBM)*. The tests were conducted with a single-cylinder engine. *DBM* was reported to produce ethylene, soot formation precursor, as direct intermediate product in combustion.

Yeh *et al.* (2001) found *isodecanol the most efficient oxygenate* in reducing particulate matter emission in a study which included various

esters, carbonates, alcohols and ethers at 2 wt-% oxygen level. In the opposite, Liotta *et al.* (1993) reported that *glycol ethers seemed to be more effective than alcohols in reducing particulate matter emission* at the same fuel oxygen level. Two *alcohols* and six *glycol ethers* in concentrations up to 5 vol-% were studied. Cetane improver was used in the blends. Oxygenates resulted in a decrease in particulate matter emission, but an increase in NO_x emission.

3.9 Carbonates



Dimethyl carbonate (DMC) is a low-molecular carbonate with boiling point of 90 °C, which is below distillation range of diesel fuel. DMC is not fully soluble in diesel fuel. Boiling point of *diethyl carbonate* is higher, 127 °C, but still lower than distillation range of diesel fuel. (Arteconi *et al.* 2011).

Karas (1994) reported of the solubility problems with *dimethyl* and *diethyl carbonates* when blended with diesel fuel. McCormick (2002) claims that *diethyl carbonate*, which can be produced from ethanol and carbon monoxide, is soluble with diesel fuel, but it has low flash point and high corrosivity. According to Karas (1994) and Liotta *et al.* (1993), solubility of *propylene carbonate* in diesel fuel is poor.

Keyu *et al.* (2002) studied a blend of *dimethyl carbonate (DMC)* and diesel fuel with a single cylinder diesel engine and a light duty diesel vehicle. A significant *reduction in exhaust submicron particles*, and a reduction of NO_x emission, was observed with DMC in the engine tests. The diesel vehicle tests indicated a significant *reduction in smoke* and CO emissions, with an increase in both HC and NO_x emissions. Huang *et al.* (2003) investigated *dimethyl carbonate* (DMC) diesel blends in a direct injection compression ignition engine. CO and *smoke emissions decreased* with increase in the DMC content, whereas no significant effect on NO_x was observed.

Kozak *et al.* (2009) reported of a study with seven glycols, two maleates and two carbonates. Oxygenates were studied with a passenger car. All oxygenates were blended as 5 vol-% concetrations in diesel fuel. Particulate matter emission was reduced with all oxygenates, whereas NO_x emission

increased in many cases. *The best PM/NO_x trade-off results were achieved with carbonates and maleates. Diethyl maleate, dimethyl carbonate* and *diethyl carbonate* were selected as the most promising oxygenates. *Dimethyl carbonate* and *diethyl carbonate*[4] were studied with light-duty vehicles by Kozak *et al.* (2008b). *Diethyl carbonate* was the most effective oxygenate to reduce particulate matter emission, when compared with *glycols* and *maleates*. Diethyl carbonate caused only a small increase in NO_x emission, therefore NO_x/PM trade-off was beneficial. However, CO and HC emissions increased.

Subramanian *et al.* (2009) studied *diethyl carbonate*, *2-ethoxy ethanol* and *diethyl ether* as diesel extender in 2.5, 5 and 7.5 wt-% blends. Diethyl carbonate was not as efficient as 2-ethoxy ethanol in terms of exhaust emissions.

Delfort *et al.* (2002) tested five carbonates together with ethers and acetals by using direct-injection diesel car. 5 vol-% addition of *diethyl carbonate, dipentyl carbonate* and two *ether carbonates* resulted in some 12 to 17% reduction in particulate matter emission over the European test cycle. For *dipentyl carbonate*, emission reduction was not as high as for other carbonates. Generally, *carbonates showed higher reductions in particulate matter emissions than ethers and acetals*. This was observed also for tetrahydrofurfuryl derivatives as 10 vol-% blends: particulate matter emission reduced with carbonate derivatives almost 30%, whereas less than 20% with alcohol, ether or acetal derivatives.

Guo *et al.* (2005) synthesised *2-ethoxyethyl carbonate* (MEEC) by introducing an ether group to dimethyl carbonate. This oxygenate was studied with a single-sylinder engine. CO emission, smoke and NO_x emissions reduced substantially, when 15 or 25 vol-% MEEC was added into diesel fuel. Viscosity of fuel decreased with addition of MEEC.

3.10 Esters, amines and amides

3.10.1 Fatty acid esters

The best-known diesel oxygenates are fatty acid methyl esters, FAME. These oxygenates are extensively studied and reported. A short summary of results is presented in this report.

[4] *Flash points of these carbonates are below 25°C.*

FAME esters are produced by a reaction of triglycerides and/or free fatty acids with alcohol using sodium or potassium hydroxide as catalyst. Side-product of process is glycerol. Methanol gives better yield than e.g. ethanol in transesterification. Various vegetable oils, animal fats, and even tall oil, can be esterified. When using rapeseed oil as a feedstock, the product is rapeseed methyl ester, RME. (Ma *et al.* 1999, Graboski *et al.* 1998).

Neat vegetable oils are not suitable for high-speed diesel engines, and thus transesterification process is required. However, even FAME esters have technical restrictions, and therefore the European diesel fuel standard EN 590:2009 limits the maximum concentration of FAME up to 7%. The requirements for FAME used for automotive fuels in Europe are defined in standard EN 14214.

Properties and performance in engine

Ignition properties of FAME esters are good with cetane numbers generally over 50. Sulphur contents of esters are low and they do not contain aromatics. In addition, lubricity of esters is good. However, the FAME biodiesel has also drawbacks. High viscosity of esters may affect injection performance and cold-start properties. Distillation range of esters is narrow and boiling point high, which may lead to dilution effect of engine oil. FAME biodiesel may contain certain impurities, e.g. triglycerides, glycerol and alcohols. Triglycerides and glycerol are viscous molecules, which can lead to carbon deposits in engine. Sodium or potassium can be present depending on the catalyst used in the esterification process. Phosphorus content of FAME depends on fertilizers used for growing plants and pressing process of vegetable oil. (Graboski et al. 1998, WWFC 2006).

FAME esters as polar compounds dissolve materials more efficiently than diesel fuel, which may lead to problems on sealing, paint, rubber and other materials with older vehicles. FAME also dissolves deposits from fuel system. Storage stability of esters is not good due to e.g. affinity of double bonds for oxidation. FAME should be used within six months after it is produced. Aged FAME can contain acids, water, peroxides, and polymerization products.

Heat content of esters is low and thus volumetric fuel consumption higher and power output of the engine lower than with diesel fuel, but this is compensated to some extent with higher density of esters. Esters are in the same hazard class as diesel, but the flash point lowers rapidly, if there is any

alcohol present as impurity. This may lead to tighter transportation and storage regulations. (Graboski et al. 1998, WWFC 2006).

Sem (2004) reported that injector deposits formed with RME in the long-term test consisted of carbon, oxygen, some metals, chlorine, phosphorus and sulphur. Many of the metals were originating from engine-wear. Deposits may originate from the decomposition of the methyl ester or glycerin molecules. The effect of phosphorus of FAME on catalyst has been studied e.g. by Krahl *et al.* (2006).

Emissions

FAME biodiesel generally reduces CO, HC and PM emissions, but increases NO_x emissions (Murtonen and Aakko-Saksa 2009, McCormick 2001, Sharp *et al.* 2000, Chang *et al.* 1997). However, these trends are not consistent as the engine, load conditions, diesel fuel used for comparison, and properties of FAME affect the results.

McCormick (2001) mentions that the reason for increase in NO_x emission with FAME is not clear, especially when considering low aromatic content of FAME. The role of density, high distillation area, oxygen content and double bonds has been considered as reasons for the increase of NO_x emission. Start of injection is earlier, and ignition delay longer when FAME is compared to high-cetane diesel fuel (McCormick 2001, Senatore et al. 2000). However, ignition delay with FAME can be shorter than that with diesel fuel, if cetane number of diesel fuel is poor. Grimaldi (2002) reported that for common-rail engine, BMEP decreases, pilot injection is smooth and main injection combustion is steep leading to high local thermal peaks contributing on generation of NO_x. Graboski (1998) commented that FAME lowers soot emission, which may increase flame temperature. In addition, changes in e.g. spray properties may cause unexpected effects. Many of the studies in 90's used low-cetane diesel fuel as a reference fuel and thus the results do not represent today's situation. Today, cetane number of conventional diesel is typically higher than cetane number of FAME, especially in Europe.

Reduction of particulate matter emission is believed to be due to presence of oxygen in FAME. (Durbin 2002, Grimaldi 2002, Grimaldi 2001, McCormick 2001). FAME reduces soot portion of particulate matter, but increases soluble organic fraction (SOF). In some cases, this can lead to higher PM emissions with FAME than with diesel fuel, e.g. at partial loads

or at cold temperatures. (Akasaka 1997, McGill 2003, Aakko 2003). Oxidation catalyst removes SOF efficiently, and thus a combination of FAME and oxidation catalyst can result in substantial benefit in PM emission.

Particle number size distributions with FAME biodiesel depend on engine, aftertreatment, load and measurement conditions. Generally, number of particles in the accumulation "soot" mode are typically lower for FAME biodiesel than for conventional diesel. However, number of accumulation mode particles in some conditions, especially at cold test temperatures, may increase due to excessive soluble organic fraction in PM. FAME diesel may increase also nuclei mode particles (Tsolakis 2006, Aakko 2003).

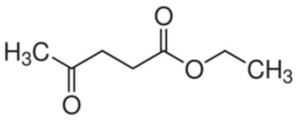
Mutagenic effect tested with Ames stest is typically lower for FAME than for fossil diesel fuel. This is believed to be due to differences in PAH content of exhaust gases. Therefore, when compared to diesel fuel with very low aromatics content, only slight or no benefit with FAME is gained as refards mutagenic effect. (Murtonen and Aakko-Saksa 2009, McGill 2003, Bünger 2007.)

As concerns toxicity, opposite results have been observed. Eckl *et al.* (1997) reported that genotoxicity with hepatocyte assay was not lower for FAME than for diesel fuel. Prieur *et al.* (2000) reported that FAME increases cytotoxicity as measured with viability parameters (ATP and GSH). On the other hand, RME prevented apoptotic phenomenon (TNF-α, nucleosome). Bünger (2000b) reported of increased toxicity on mouse fibroblasts at idling, but not at rated power, when compared to diesel fuel. Also rat tests have been conducted with FAME biodiesel (Finch *et al.* 2000).

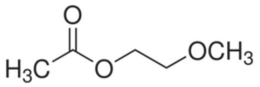
Typically oxygen containing fuels tend to increase aldehyde emissions, and many studies, e.g. Krahl *et al.* (2001), report of increase in aldehyde emissions with FAME biodiesel. Some studies report also on reductions of aldehyde emissions with FAME, but in these cases (e.g. Sharp 2000b) very low-cetane diesel fuel has been used as reference fuel. Opposite results have been obtained as well (Murtonen and Aakko-Saksa 2009). Engine type and cetane number of reference diesel fuel may affect the results.

3.10.2 Other esters

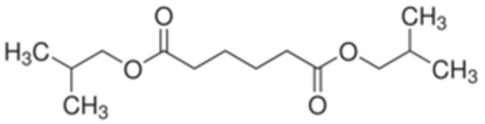
Ethyl levulinate can be produced from cellulosic materials through levulinic acid (4-oxo-pentanoic acid). Biofine Inc. is developing this process. Cetane number of neat ethyl levulinate is poor, below 10. However, cetane number of diesel fuel remains acceptable in 5 and 10 vol-% blends. (McCormic 2002).



Ethyl levulinate



2-Methoxyethyl acetate



Di-isobutyl adibate

Yanfeng *et al.* (2007) reported of the tests with a 20% blend of *2-methoxyethyl acetate (MEA)*[5] in diesel fuel. Single-cylinder engine tests were carried out. With this oxygenate, the ignition delay and duration of combustion shortened. MEA reduced smoke, CO and HC emissions, but only little effect was seen on NO_x emission. MEA can be synthetized by acetic acid and ethylene glycol monomethyl ether.

Hilden *et al.* (2001) studied *di-isobutyl adibate* and *di-butyl phthalate* as diesel extenders. From these oxygenates, di-isobutyl adibate was the most effective in the reduction of the exhaust emissions, whereas aromatic oxygenate was the worst one.

Lin and Huang (2003) investigated the effect of the *ethylene glycol mono-acetate* on engine performance and emission characteristics in marine diesel engines. Ethylene glycol mono-acetate decreased NO_x, CO and CO_2 emissions, but increased brake-specific fuel consumption.

[5] **Synonyms:** EGMEA; Ethylene glycol monomethyl ether acetate; Glycol monomethyl ether acetate; 2-Methoxyethanol acetate; Methyl Cellosolve® acetate.

3.10.3 Amines and amides

Stournas (1993) studied amides (R-C(=O)NR´R´´) and amines (R-NH_2), which were processed from fatty acids[6]. Blending cetane numbers of these fatty acid derivatives are high (Figure 3.5). Serdari *et al.* (2000) reported of using tertiary fatty amides as diesel fuel substitutes. Blending cetane numers of 15 amides tested varied from some 80 to 100, when calculated with blends containing 10% amides in diesel fuel. Tertiary fatty acid amides contain oxygen, which should lead to improved combustion. Exhaust emissions were measured with Petter engine using three amides as 5% concentration in diesel fuel. Particulate matter emissions reduced with three amides tested.

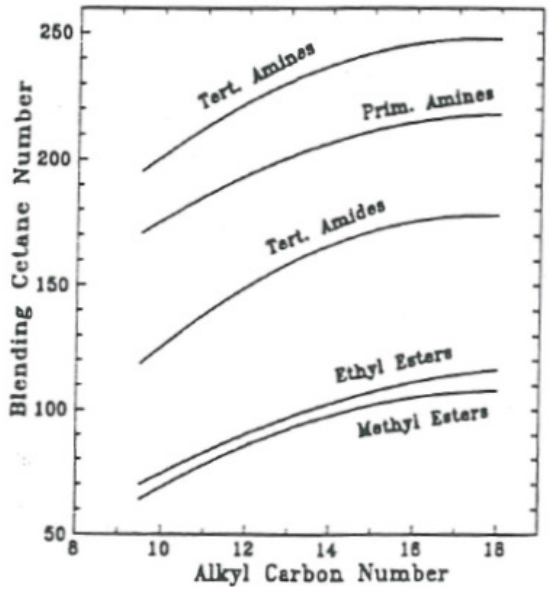


Figure 0.8. Blending cetane number of fatty acid derivatives (Stournas *et al.* 1993).

[6] Nitrogen in amines and amides may substantially increase NO_x emissions, if used as diesel fuel component. For example, 1% nitrogen content in fuel would lead to some 6.5 g/kWh NO_x emission with certain assumptions (Editorial).

4. Oxygenate selection for experimental part

In the "Refuel" project coordinated by Aalto University, diesel fuel oxygenate was selected for the engine tests of the experimental part. The preliminary screening was reported by Tilli *et al.* (2010).

In principle, a large number of oxygenates could be used as fuels or diesel fuel components. Many studies have covered a comprehensive set of oxygenates, and some oxygenates are reported as promising blending components for diesel fuel. However, many oxygenates are addressed with end-use problems e.g. poor solubility with diesel fuel or safety problems. In addition, economic feasibility of oxygenates may be challenging.

In this review, the following criteria were used in the selection of diesel oxygenates for engine tests:

- Ignition quality: cetane number minimum 51
- Flash point: above 55 °C
- Boiling point: close to range of 180-340 °C
- Solubility in diesel fuel: soluble in diesel fuel

The target oxygen content of the blend in the experimental part was set to 2-3 wt-%. This means that components with oxygen content of 10 wt-% can be used without increasing blending ratio over 20%, for example.

Oxygenates, which were selected to closer review, and all oxygenates evaluated as candidates are listed in the end of this Appendix. Glycol ether (TPGME) and maleate (DBM) have been studied extensively in 2000's representing candidates containing over 35 wt-% oxygen (Natarajan et al. 2001). DBM was excluded from the study at hand due to cetane number below 50. TPGME was excluded due to phase separation risk in certain conditions (if water is present, at high blending ratios, with paraffinic fuel, at low temperatures) (Natarajan 2001, Murphy 2002). Some interesting options, such as ethoxy ethyl ether and butylal, were not commercially available.

VTT has experience on of di-n-pentyl ether (DNPE) as diesel oxygenate (for example Martin *et al.* 1997). DNPE performed well in the earlier engine

tests at VTT. Emission behavior was good also based on literature (Chapter 3.3.3). In addition to particulate matter emission, DNPE has been capable to reduce also other emission species, even NO_x emissions. Finally, di-n-pentyl ether was selected as oxygenate for the experimental part of "Refuel" project.

5. Summary

Oxygenates are considered as diesel fuel components, because they are capable of reducing exhaust emissions. Oxygenates based on renewable feedstocks would also help with climate change and energy security challenges. *In this study, the objective is to cover oxygenates, which are compatible with conventional diesel engines, and which effectively reduce particulate matter emissions.* Combination of paraffinic fuel and oxygenates could lead to very low particulate matter emissions.

For diesel engine, NO_x and particulate matter emissions are bottlenecks. These emissions can be reduced by using emission control devices and/or by using tailored fuels. Generally, oxygenates reduce particulate matter emission. There are indications of 3-15% or even 67% reduction in particulate matter emissions with 1% oxygen content in fuel. A number of mechanisms have been presented to explain this effect. A general theory is that oxygenated fuels bring oxygen in the combustion process, which reduces soot formation. Theory may vary with different oxygenates, and the role of oxygen entrained from ambientmay be significant, as well as the role of engine and load, for example. Many studies emphasise the role of the functional group of oxygenate, even though the results are not consistent.

A number of different oxygenates, for example alcohols, ethers, esters and carbonates, are considered as diesel fuel components. Oxygenates are polar in nature, whereas hydrocarbons are non-polar compounds, which may lead to various compatibility problems. Many fuel properties of oxygenates need consideration when evaluated as diesel fuel components, e.g. cetane number, flammability, volatility, density, viscosity and lubricity. The best-known diesel oxygenates today are FAME ester. Light oxygenates are not compatible with diesel fuel. Heavier alcohols, ethers and acetals are considered promising diesel components.

Based on the literature, diesel fuel oxygenate was selected for the engine tests of the experimental part. The following criteria were used in the selection of diesel oxygenates for engine tests: cetane number minimum 51; flash point above 55 °C; boiling point close to 180-340 °C; soluble in diesel fuel. The target oxygen content of the blend was set to 2-3 wt-%. Almost 140 oxygenates were evaluated. Examples of the rejected oxygenates are dibutyl

maleate (low cetane number) and glycol ether TPGME (phase separation risk). Some oxygenates, for example ethoxy ethyl ether and butylal, were not commercially available. Finally, di-pentyl ether (DNPE) was selected as oxygenate for the experimental part of "Refuel" project. DNPE has performed well in the emission tests, fuel properties are diesel-like, and DNPE is also commercially available.

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Appendix 2.1: Oxygenate candidates selected for final review

		MW	Oxygen wt-%	Flash point °C	Boiling point °C	Density kg/dm^3	Cetane number	Note	Reference
ALCOHOLS									
1-dodecanol, lauryl alcohol	C12H26O	186	8.6	127	259	0.831	64 [b]	Melting point 24 °C.	b
1-tetradecanol, myristyl alcohol	C14H30O	214	7.5	145	>260	0.824	51/81 [b]	Melting point 38 °C.	b
1-octadecanol, stearyl alcohol	C18H38O	270	5.9	195	~330	0.810	81 [b]	Melting point 55 °C.	b
ETHERS									
2-Ethoxy ethanol	C4H10O2	90	35.6	54	135	0.930	58	Low boiling point.	a, z
Di-n-butyl ether	C8H18O	130	12.3	25	141	0.767	85, 91 [b], 100 [b], 91-100 [k]; 147 [c]	Flash point fails.	c, e, l
Hexyl methyl ether	C7H16O	116	13.8	23	126	0.770	97 [b]	Flash point fails.	b
n-Pentyl ether, DNPE	C10H22O	158	10.1	57	187	0.783	111-130 [f], 109, 103-153 [n]		d, f, k, l, n
Di-n C6-8-ethers	group	group	<10				116		l
Dibutoxy methane (Butylal)	C9H20O2	160	20.0	62	180	0.8354	>74	Problems?	c, d, f
Dipentoxy methane	C11H24O2	188	17.0		218	0.841	97, 120 [c]	CFPP -7°C	k
Diethoxy 1.1-propane	C7H16O2	132	24.2	10?			136	Flash point fails.	c
Diethoxy butane	C8H18O2	146	21.9	45	143	0.841	96.6 [b], 97 f; 128 [c]	Flash point fails.	b, c, f, m
Dibutoxy 1.1-butane	C12H26O2	186	17.2				134		c
Diethoxy 1.1-pentane; valeraldehyde diethyl acetal	C9H20O2	160	20.0	36	163		124	Flash point fails.	c
Dipentoxy 1.1-pentane	C15H32O2	244	13.1				130		c
Dimethoxyhexane	C8H18O2	146	21.9				88 [b]		b
2,4,7,9-Tetra-oxa-decane (TOD)	C6H14O4	150	42.7	68	175	1.005	58 [b]	Toxicity suspected	b, p
Polyacetals, 4 compounds	group	group					119, 127, 132, 136		c
Poly-oxy-methylenes, Snamprogetti	group	group					80-100		s
GLYCOL ETHERS									
Ethylene glycol dimethyl ether, Dimethoxyethane (Glyme)	C4H10O2	90	35.6	-6	85 [g]	0.8683	90-98 [b, e]	Flash point fails.	e, g, h
Diethylene glycol dimethyl ether (Diglyme)	C6H14O3	134.2	35.8	67, 51 [g]	162 [g]	0.945	112 [g], 120 [y]	Health concerns?	e, g, h, q, y
Diethylene glycol diethyl ether, 2-Ethoxy ethyl ether, Ethyl diglyme, Diethyl diglycol, Diethyl carbitol	C8H18O3	162	29.6	54[m], 71	189	0.91	86 [m], 113-136	Poor lubricity, corrosion?	d, e, f
Diethylene glycol dibutyl ether	C12H26O3	218	22.0	120	256	0.884	144 [g]	Not soluble, phase separatic	g, h
Triethylene glycol mono-methyl ether	C7H16O4	164	39.0	118		1.026	75 [b]	Not soluble, phase separatic	b
Triethylene glycol dimethyl ether (Triglyme)	C8H18O4	178	36.0	111, 113 [g]	220 [g]	0.986	>75, 120 [i,j], 144 [g]	Corrosion problems?	g, h, i, j, t
Tetraethylene glycol dimethyl ether (Tetraglyme)	C10H22O5	222	36.0	140, 141 [g]	275	.009, 1.010	144 [g]	Not soluble, phase separatic	g, h
Dipropylene glycol dimethyl ether	C8H18O3	162	29.6	65	175	0.903	86 [g]	Not soluble, phase separatic	g
Tripropylene glycol methyl ether (TPGME)	C10H22O4	206	31.1	>110 [h]	242	0.96	65, 74.5 [i,j]	Not soluble in paraffins.	d, h, i, j, o, r, t
CETANER (20% monoglyme 80% diglyme)	group	group					128 [c]		c, o, v
CARBONATES									
Dipentyl carbonate, diamyl carbonate	C11H22O3	202	23.8				142		c
Di(ethoxy-2-ethyl) carbonate	C9H18O5	206	38.8			1.04	98		c
Di(diethoxy-2-ethyl)carbonate	C13H26O7	294	38.1			1.02	136		c
ESTERS									
Ethyl decanoate	C12H24O2	200	16.0	102	241	0.863	51/60 [b]	Melting point -20 °C.	b
Propyl decanoate	C13H26O2	214	15.0	109	253	0.85	53,64 [b]		b
Butyl decanoate	C14H28O2	228	14.0	120	274	0.858	54, 63 [b]		b
Decyl acetate	C12H24O2	200	16.0	>110	272	0.862	62 [b]		b
Methyl laurate	C13H26O2	214	15.0	>110	261	0.866	54-70 [b]	Melting point 4 °C.	b
Ethyl laurate	C14H28O2	228	14.0	100	269	0.858	73 [b]	Melting point -12 °C.	b
Dodecyl ethanoate, lauryl acetate	C14H28O2	228	14.0	>100	150	0.865	77 [b]		b
Methyl myristate, Methyl tetradecanoate	C15H30O2	242	13.2	>110	323	0.855	66-74 [b]	Melting point 18 °C.	b
Decyl valerate, propyl laurate, ethyl myristate	C15H30O2	242	13.2	130	290	0.859	67-72 [b]		b
Valeric biofuels, pentyl valerate	C10H20O2	172	18.6	75	207/190	0.874	suitable		u
AMIDES									
Tertiary fatty amides	group	group	group				90-250 for 15 compounds		x

[a] Natarajan et al. 2001 [b] Murphy et al. 2004 [c] Delfort et al. 2002 [d] Murphy 2002 [e] Bertoli et al. 1997 [f] Nylund et al. 2005 [g] Kozak et al. 2007 [h] Kozak et al. 2009 [i] Boot 2007 [j] Boot 2009 [k] Giavazzi et al. 1991 [l] Pecci et al. 1991 [m] McCormic et al. 2002 [n] Marchionna 2000 [o] Smith et al. 2008 [p] Naegeli et al. 2001 [q] Nabi et al. 2010 [r] Gonzales et al. 2001, [s] Hart 2001 [t] Frijters et al. 2006 [u] Lange et al. 2010 [v] Hess et al. 2000 [x] Stournas et al. 1993 and Sedari et al. 2000 [y] Loganathan 2007 [z] Subramanian 2009

Appendix 2.2: List of oxygenate candidates in evaluation

Substance	Note	CN	Reference
Diesel fuel***		>51	
Alcohols			
Methanol	Low flash point		a, f
Ethanol	Low flash point	8	a, f
t,n and/or i-Butanols	Low flash point		a, ö, aa
1-decanol		50	b, å
Isodecanol			z
1-undecanol		53	b
1-dodecanol	Melting point 24 °C	64	b
1-tetradecanol	Melting point 38 °C	51, 81	b
1-hexadecanol		51	b
1-octadecanol	Melting point 55 °C	81	b
Biodiesel 15 (Agrodiesel 15), commercial in Sweden	Group of oxygenates		ab
Ethers			
Dimethyl ether (DME)	Low flash point		a
Diethyl ether (DEE)	Low flash point	62	ac, z
Methyl tertiary butyl ether, MTBE	Low flash point		a
Di-n-butyl ether	Low flash point	85-147	c, e, l
Hexyl methyl ether	Low flash point	97	b
n-Pentyl ether, DNPE		103-153	d, f, k, l, n
Di-n C6-8-ether		116	l
Methoxy ethanol			a
2-Ethoxy ethanol	Not soluble	58	a, ac
2-Butoxy ethanol			a
1-Methoxy-2-propanol	Low flash point	low	a, r
Anisole, methoxybenzene			z
Acetals (2 oxygen bonds with one carbon), other ethers			
Dimethoxymethane, Methylal (DMM)		..49-58	a
Dimethoxyacetal (DMA), 1,1-dimethoxyethane			a
Diethoxy methane, Ethylal (DEM)	Low flash point		a
Di-propoxy methane, n-Propylal	Low flash point		a
Di-isopropoxy methane, Isopropylal	Low flash point		a
Dibutoxy methane (Butylal)		>74	a, c, d, f
Di-pentoxy methane	CFPP -7 °C	97, 120	k

Diethoxyethane, "acetal"	Low flash point		ad
Dibutoxy methane			
Diethoxy 1.1-propane		136	c, d, f
1.1.3.3-Tetramethoxypropane	Corrosion, toxicity?		a
1.1.3.3-Tetraethoxypropane	Corrosion		
Diethoxy butane	Low flash point	97, 128	b, c, f, m
Dibutoxy 1.1-butane		134	c
Diethoxy 1.1-pentane	Low flash point	124	c
Dipentoxy 1.1-pentane		130	c
Dimethoxyhexane		88	b
2.4.7.9-Tetra-oxa-decane (TOD)	Poor lubricity, toxicity?	58	a, b, p
2.5.7.10-Tetra-oxa-undecane (TOU)	Not soluble, toxicity?		a
Acetal from glycerin (2.2-dimethyl-1.3-dioxolan-4yl)methyl acetate			ae
Polyacetals, 4 compounds		119-136	c
Poly-oxy-methylenes, Snamprogetti		80-100	s, af
branched C4-C6-diethers		42-75	l
Di-2-ethoxy-2ethyl ether			c, r
2-Ethoxy ethyl ether			a, m
Trioxane (cyclic ether)			a, z
Trimethoxymethane			z
Glycerol-t-butyl ether (GTBE)			a, i, ä
Di-Butoxy glycerol (DBG)			ag
Glycol ethers			
Ethylene glycol dimethyl ether, Dimethoxyethane (Glyme)	Low flash point	90-98	a, e, g, h
Ethylene glycol mono n-butyl ether			ah
Ethylene glycol di-t-butyl ether			ah
Ethylene glycol monoethyl ether acetate, 2-Ethoxy ethyl acetate	Engine problem[r], toxicity?	40	a, r
Diethylene glycol	Not soluble, toxicity?		a
Diethylene glycol mono-methyl ether	Not soluble, toxicity?		a
Diethylene glycol mono-ethyl ether	Not soluble, toxicity?		
Diethylene glycol dimethyl ether (Diglyme)	Water tolerance, toxicity?	112, 120	a, e, g, h, q, y, z

Diethylene glycol diethyl ether, 2-Ethoxy ethyl ether (Diethyl diglycol, Diethyl carbitol)	Poor lubricity, corrosion?	113-136	a, d, e, f
Diethylene glycol ethyl ether acetate	Not soluble, toxicity?		a
Diethylene glycol dibutyl ether	Not soluble or phase separation	144	g, h
Triethylene glycol mono-methyl ether	Not soluble, toxicity?	75	a, b
Triethylene glycol dimethyl ether (Triglyme)	Corrosion, toxicity?	120, 144	a, g, h, i, j, t
Triethylene glycol mono-ethyl ether, Ethoxy triglycol	Toxicity?		
Tetraethylene glycol dimethyl ether (Tetraglyme)	Not soluble, toxicity?	144	a, g, h
Dipropylene glycol mono-methyl ether	Not soluble, phase separation, engine problem [r]	42, 44	a, b, r
Dipropylene glycol dimethyl ether	Not soluble, phase separation	86	g
Tripropylene glycol methyl ether (TPGME)	Not fully soluble with FT, water phase separation	65, 75	a, d, h, i, j, o, r, t
CETANER (20% monoglyme 80% diglyme)		128	c, o, v
Carbonates			a
Dimethyl carbonate	Solubility problem [ä]	10, 35-36	h, ä, ai
Diethyl carbonate	Corrosion, solubility problem	14, 54, 57	a, c, h, ä, ai
Dipropyl carbonate	Soluble, corrosion		a, z
Dibutyl carbonate		39	c
Dipentyl carbonate		142	c
Di(ethoxy-2-ethyl) carbonate		98	c
Methyl-2-ethoxyethyl carbonate (valmistettu DMC:stä)			aj
Di(diethoxy-2-ethyl)carbonate		136	c
Tetramethoxy ortho carbonate	Not soluble or phase separation		a
Propylene carbonate			
Esters			
FAME		>50	
Dimethyl maleate	Not soluble or phase separation		a
Diethyl maleate (DEM)	Not soluble or phase separation		a, d, h

Dibutylmaleate (DBM)	Soluble	28, <50	a, d, h, i, o, r, t, ak
Diethylene glycol diacetate	Not soluble, toxicity?		a
Tributyrin	Soluble		a, r
Trimethyl orthoformate	Flash point fails		a
Methyl acetate			a
Ethyl acetate			a
Ethylene glycol monoacetate			al
Ethylene glycol diacetate	Not soluble, toxicity?		
2-Methoxy acetate	Fail		
Isopropyl acetate	Fail		a
3-Methoxybutyl acetate (Butoxyl)	Not soluble, toxicity?		a
2-Methoxyethyl acetate (MEA)			a, am
Ethyl aceto acetate (acetoacetic ester)	Not soluble, toxicity?		a
2-Butoxyethyl acetate	Soluble, corrosion		a
Diacetin, glycerol diacetate	Not soluble or phase separation		a
Glycerol-tributrate (butanoic acid 1,2,3-propanetriyl ester)			ai
Isopropyl lactate	Not soluble or phase separation		a
Butyl lactate	Soluble, corrosion		a
Dimethyl succinate	Not soluble or phase separation		a
Diethyl succinate (Butanedioic Acid, Diethyl Ester)	Not soluble or phase separation		a
Triethyl citrate	Not soluble or phase separation		a
Dimethyl malonate	Not soluble or phase separation		a
Diethyl malonate	Not soluble or phase separation		
Dimethyl adipate	Not soluble or phase separation		a
Diethyl adipate	Toxicity?	15	a, b, r
Di-isopropyl adibate			z
Di-isobutyl adibate			an
Di-butyl phthalate			an
Ethyl decanoate	Melting point -20 °C	51, 60	b
Propyl decanoate		53, 64	b
Butyl decanoate		54, 63	b
Decyl acetate		62	b
Methyl laurate	Melting point 4 °C	54-70	b
Ethyl laurate	Melting point -12 °C	73	b
Dodecyl ethanoate		77	b

Methyl myristate, Methyl tetradecanoate	Melting point 18 °C	66-74	b
Decyl valerate, propyl laurate, ethyl myristate		67-72	b
Valeric biofuels		>50	u
Pentyl valerate			u
Ethyl levulinate		<10	m
"Furanics", e.g. hydroxymethyl furfural (HMF)			ao
Tetrahydrofurfuryl alcohol	Not soluble or phase separation		a
Complex alcohol esters			z
Others			
Cyclohexanone		10	j
Tertiary fatty amides		90-250	x
Tert-butyl peroxyacetate			ap
Acetaldehyde			a
Acetyl acetone	Flash point fails		a
Trimethyl acetic acid	Soluble		a
Butanal, butyraldehyde			a
Propanal, propionaldehyde			a

[a] Natarajan et al. 2001, [b] Murphy et al. 2004, [c] Delfort et al. 2002, [d] Murphy 2002, [e] Bertoli et al. 1997, [f] Nylund et al. 2005, [g] Kozak et al. 2007, [h] Kozak et al. 2009, [i] Boot 2007, [j] Boot 2009, [k] Giavazzi et al. 1991, [l] Pecci et al. 1991, [m] McCormic et al. 2002, [n] Marchionna 2000, [o] Smith et al. 2008, [p] Naegeli et al. 2001, [q] Nabi et al. 2010, [r] Gonzales et al. 2001, [s] Hart 2001, [t] Frijters et al. 2006, [u] Lange et al. 2010, [v] Hess et al. 2000, [x] Stournas et al. 1993 and Sedari et al. 2000, [y] Loganathan 2007, [z] Yeh et al. 2001,[å] Janssen 2009, [ä] Karas 1994, [ö] Zöldy 2010, [aa] Wadumesthrige 2010, [ab] Golubkov 2005, [ac] Subramanian 2009, [ad] Nord 2005, [ae] Garcia 2008, [af] Lumpp 2011, [ag] Spooner-Wyman, [ah] Nabi 2002, [ai] Kozak 2008, [aj] Guo 2005, [ak] Mueller 2003, [al] Lin and Huang 2003, [am] Yangfeng 2007, [an] Hilden 2001, [ao] de Jong 2009, [ap] Cunningham 1995

In the field of transport power units, the traditional diesel- and otto-cycles have been developed since late 19th century. The aim of the development work has been to optimize the processes for crude oil based gasoline and diesel fuel. The awareness of the effect of the carbon dioxide emissions on the global warming and the limited resources of crude oil in the future have put the bioderived renewable fuels in special interest. This domestic three-year (2009-2011) project, Future Combustion Technology for Synthetic and Renewable Fuels in Compression Ignition Engines (ReFuel), was a joint research project with Aalto University (Aalto), Tampere University of Technology (TUT), Technical Research Centre of Finland (VTT) and Åbo Akademi University (ÅAU) in Finland.

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